A NOTEBOOK FOR TOPICS IN THERMODYNAMICS OF SOLUTIONS AND LIQUID MIXTURES



Michael J Blandamer & Joao Carlos R Reis
University of Leicester & Faculdade de Ciencias

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A Notebook for Topics in Thermodynamics of Solutions and Liquid Mixtures

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Licensing

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Preface

Over three hundred Topics in Thermodynamics (which can addressed individually) describe the thermodynamic properties of aqueous solutions and aqueous mixtures. The Gibbs energies of these systems are discussed leading through successive differential operations to enthalpies, volumes, heat capacities, compressibilities (isobaric and isentropic) and expansibilities. These properties are linked quantitatively to corresponding partial molar properties including chemical potentials and generally partial molar volumes, partial molar enthalpies, partial molar heat capacities, partial molar expansibilities and compressibilities. Key equations link experimentally determined variables (e.g. densities) and partial molar properties (e.g. partial molar volumes) of the components in an aqueous solution/mixture. Extensive references are given to published papers describing application of the equations described in The Topics.

Further Topics describe application of thermodynamic equations to descriptions of chemical equilibria for many classes of systems together with the dependences of equilibrium constants on temperature and pressure. The analysis is extended to a consideration of rate constants for chemical reactions between solutes in solution.

The theoretical basis is described for the Debye-Huckel treatment of salt solutions, Bjerrum equation for ion association, Euler's theorem, Legendre (thermodynamic) transformations, Lewisian variables, L'Hospital's Rules. Related Topics describe electrical units, axioms , equilibrium and frozen properties.

In each Topic, special attention is given to the units of parameters involved in equations, ensuring that the derived property has self consistent units as required in the SI system. Related Topics describe electrical units, axioms and both equilibrium and frozen properties. The thermodynamic analysis is extended to a consideration of several special Topics including thermodynamic stability, the Law of Mass Action, Adsorption, Isochoric and Equilibrium properties, extrathermodynamic analysis of acid strengths and solvent polarities, Hildebrand Solubility parameters, internal pressure of liquids, ion association, surfactants, Gibbs Adsorption Isotherm, Phase Rule, thermal stability and hydrogen ions in aqueous systems.

In the context of quantitative description of aqueous systems, key references are given to the properties of water including molar volume, viscosity, relative permittivity and self-dissociation.

Cross references are given to relevant subject matter in other Topics.

CHAPTER OVERVIEW

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1.1.1: Acid Dissociation Constants- Weak Acids- Debye-Huckel Limiting Law

For a weak acid HA in aqueous solution at temperature T and pressure p (which is ambient pressure and so close to the standard pressure) the following chemical equilibrium is established.

$$\mathrm{HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq)}$$

The r.h.s. of equation (1.1.3) describes a 1:1 'salt' in aqueous solution. At equilibrium (i.e. at a minimum in Gibbs energy), the thermodynamic description of the solution takes the following form.

$$\mu^{eq}(\mathrm{HA; aq; T; p}) + \mu^{\mathrm{eq}}\left(\mathrm{H_2O; aq; T; p}\right) = \mu^{\mathrm{eq}}\left(\mathrm{H_3O^+A^-; aq; T; p}\right)$$

We express $\mu^{eq}(H_2O;aq;T;p)$ in terms of the practical osmotic coefficient φ for the solution.

$$\mu^{eq}\left(\mathrm{H_2O; aq; T; p}\right) = \mu^{*}\left(\mathrm{H_2O}; \lambda; \mathrm{T; p}\right) - \phi\,\mathrm{R\,T\,M_1}\,\left[\mathrm{m(HA)} + 2\,\mathrm{m_j}\right]^{eq}$$

Here m_j is the molality of the 'salt' $H_3O^+A^-$. The latter yields 2 moles of ions for each mole of $H_3O^+A^-$. A full description of the solution takes the following form.

$$\begin{aligned}\mu^0(\mathrm{HA; aq}) + \mathrm{R\,T\,ln}\left[\mathrm{m(HA)}\,\gamma(\mathrm{HA})/\mathrm{m^0}\right]^{eq} \\ + \mu^{*}\left(\mathrm{H_2O}; \lambda\right) - \phi\,\mathrm{R\,T\,M_1}\,\left[\mathrm{m(HA)} + 2\,\mathrm{m_j}\right]^{\mathrm{eq}} \\ = \mu^0\left(\mathrm{H_3O^+A^-; aq}\right) + 2\,\mathrm{R\,T\,ln}\left[\mathrm{m_j}\,\gamma_{\pm}\right]^{\mathrm{eq}}\end{aligned}$$

The practical osmotic coefficient φ describes the properties of solvent, water in the aqueous solution; $\gamma_\pm$ is the mean ionic activity coefficient for the 'salt' $H_3O^+A^-$. By definition, if ambient pressure p is close to the standard pressure p^0, the standard Gibbs energy of acid dissociation,

$$\begin{aligned}\Delta_{\mathrm{d}}\mathrm{G}^0 = \mu^0\left(\mathrm{H_3O^+A^-; aq; T; p}\right) - \mu^0(\mathrm{HA; aq; T; p}) - \mu^0\left(\mathrm{H_2O}; \lambda; \mathrm{T; p}\right) \\ = -\mathrm{R\,T\,ln}\left(\mathrm{K_A^0}\right)\end{aligned}$$

$\mathrm{K_A^0}$ is the acid dissociation constant. Combination of equations (1.1.4) and (1.1.5) yields equation (1.1.6).

$$\mathrm{K_A^0} = \frac{\left[\mathrm{m}\left(\mathrm{H_3O^+\,A^-}\right)^{\mathrm{eq}}\,\gamma_{\pm}\left(\mathrm{H_3O^+A^-}\right)^{\mathrm{eq}}/\mathrm{m^0}\right]^2\,\exp\left[\phi\,\mathrm{M_1}\,\left(\mathrm{m(HA)} + 2\,\mathrm{m_j}\right)\right]^{\mathrm{eq}}}{\left[\mathrm{m(HA)}\,\gamma(\mathrm{HA})/\mathrm{m^0}\right]^{\mathrm{eq}}}$$

For dilute aqueous solutions, several approximations are valid. The exponential term and $\gamma(HA)^{eq}$ are close to unity. There are advantages in defining a quantity $\mathrm{K_A^0}$ (app) . Further, $\gamma_\pm(H_3O^+A^-)$ is obtained using the Debye - Huckel Limiting Law, DHLL.

By definition,

$$\mathrm{K_A(app)} = \left[\mathrm{m}\left(\mathrm{H^+A^-}\right)^{\mathrm{eq}}\right]^2/\mathrm{m(HA)^{eq}\,m^0}$$

Then

$$\mathrm{ln\,K_A(app)} = \mathrm{ln\,K_A^0} + 2\,\mathrm{S_\gamma}\left(\mathrm{I/m^0}\right)^{1/2}$$

In other words, with increase in ionic strength I, $\mathrm{K_A(app)}$ increases as a consequence of ion - ion interactions which stabilize the dissociated form of the acid.

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1.1.2: Acquisitive Convention

This convention refers to the sign associated with communication between a system and its surroundings. The convention describes changes as seen from the standpoint of the system. The convention guides chemists concerning the ‘sign’ of changes in thermodynamic variables

00for a given system. For example, if heat q flows from the surroundings into a system, q is positive. If thermodynamic energy U is lost by a system to the surroundings, ΔU is negative. In fact this convention is intuitively attractive to chemists. For example, when told that the volume of a system increases during a given process, then chemists conclude that the volume of the surroundings (i.e. the rest of the universe!) decreases.

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1.1.3: Activity- Solutions and Liquid Mixtures

The concept of activity was introduced by Lewis[1] in descriptions of the properties of liquid mixtures and solutions. By way of illustration we consider the chemical potential of chemical substance j, $\mu_j(\text{ system })$ present in a solution at fixed pressure p and temperature T. By definition,

$$\mu_j(\text{ system }) = \mu_j(\text{ ref }) + RT\ \ln(a_j)$$

While we can never know either $\mu_j(\text{ system })$ or $\mu_j(\text{ ref })$, the difference is related to the activity a_j, a dimensionless function of the composition of the system. We as observers of the system are required to define the reference state where the chemical potential of chemical substance j can be clearly defined. Nevertheless the terms $\mu_j(\text{ system })$, $\mu_j(\text{ ref })$ and a_j in equation (a) are based on somewhat abstract concepts. The link with practical chemistry is made through the differential of equation (a) with respect to pressure at constant temperature.

$$\text{Then, } \mathrm{V_j(\text{ system }) = V_j(\text{ ref }) + R\,T\ [\partial \ln(a_j)/\partial p]_T}$$

$\mathrm{V_j(\text{ system })}$ and $\mathrm{V_j(\text{ ref })}$ are, respectively, the partial molar volumes of chemical substance j in the system and in a convenient reference state. The term $\mathrm{R\,T\ [\partial \ln(a_j)/\partial p]_T}$ contrasts the role of intermolecular interactions in the two states. Four applications of the concept of activity make the point.

For the binary liquid mixture, ethanol + water at defined temperature and pressure, the activity of, for example, water (substance 1) a_1 is given by the product, $x_1\,f_1$ where f_1 is the (rational) activity coefficient and x_1 is the mole fraction of water.

$$a_1 = x_1\,f_1$$

The activity of urea (chemical substance j) in an aqueous solution is related to the product of activity coefficient γ_i and molality m_j using the reference molality m^0, namely $1\mathrm{molkg^{-1}}$.

$$a_j = \left(m_j/m^0\right)\,\gamma_j$$

If the concentration of urea in the solution equals $c_j\mathrm{moldm^{-3}}$, then the activity a_j is given by equation (e) where c_r is the reference concentration c_r, $1\mathrm{moldm^{-3}}$, and y_j is the solute activity coefficient.

$$a_j = (c_j/c_r)\ y_j$$

If x_j is the mole fraction of urea and $\mathrm{f_j^*}$ is the asymmetric activity coefficient, the activity of urea is given by equation (d).

$$a_j = x_j\,f_j^*$$

Equations (d) to (f) describe the same property, namely activity a_j of solute j in a given solution.

Footnotes

[1] G. N. Lewis, Proc. Am. Acad. Arts Sci.,1907,43,259.

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1.1.4: Activity of Aqueous Solutions

A given aqueous solution is prepared using 1 kg of water(λ, molar mass $\mathrm{M_1}$, and m_j moles of solute at temperature T and pressure p (which is close to the standard pressure p_0) At fixed T and p, the activity of water $a_1(\mathrm{aq})$ is related to the chemical potential of water in the aqueous solution using equation (a) where $\mu_1^*(\lambda)$ is the chemical potential of water(λ) at the same T and p.

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) + \mathrm{R\,T\,ln\,(a_1)}$$

Further equation (b) relates $\mu_1(\mathrm{aq})$ to the molality of a simple solute, m_j (e.g. urea) where R is the gas constant ($= 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$).

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \phi\,\mathrm{R\,T\,M_1\,m_j}$$

Here m_j is the molality of solute j and ϕ is the practical osmotic coefficient. If the thermodynamic properties of the aqueous solution are ideal (i.e. no solute-solute interactions) the practical osmotic coefficient is unity.

$$\mathrm{At\ fixed\ T\ and\ p, limit\ (m_j \to 0)}\ \phi = 1.0$$

$$\mathrm{Hence,}\ \mu_1(\mathrm{aq;id}) = \mu_1^*(\lambda) - \mathrm{R\,T\,M_1\,m_j}$$

Therefore in the case of an ideal solution, addition of a solute, molality m_j, stabilises the solvent; i.e. lowers the chemical potential of the solvent. In the event that solute j is a salt which forms with complete dissociation ν ions for each mole of salt in solution, $\mu_1(\mathrm{aq})$ is given by equation (e).

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \mathrm{v}\,\phi\,\mathrm{R\,T\,M_1\,m_j}$$

We consider an aqueous solution containing a simple neutral solute j. In order to understand the properties of this solution, we need to consider water-solute interactions and solute j – solute j interactions. Solute-solute interactions determine the extent to which the properties of a given solution differ from those of the corresponding solution having thermodynamic properties which are ideal [1].

The extent to which the thermodynamic properties of solutions are not ideal also reflects in part the role of water-solute interactions. For example the extent to which urea-urea interactions differ from ethanol-ethanol interactions in aqueous solutions reflects the different hydration characteristics of urea and ethanol.

Comparison of equations (a) and (b) yields the following important equation relating activity of solvent, water, and the molality of simple neutral solute j.

$$\mathrm{Thus,}\quad \mathrm{ln\,(a_1)} = -\phi\,\mathrm{M_1\,m_j}$$

The minus signs in equations (b) and (f) are extremely significant. If the thermodynamic properties of the solutions are ideal, ϕ is unity.

$$\mathrm{Then,\ ln\,(a_1)^{id} = -M_1\,m_j = -M_1\,n_j/n_1^0\,M_1 = -n_j/n_1^0}$$

Here $n_1{}^0$ is the amount of solvent, water, molar mass $\mathrm{M_1}$; n_j is the amount of solute j. Therefore a plot of $\mathrm{ln\,(a_1)^{id}}$ against molality m_j is linear with slope '$-\mathrm{M})1$'. Furthermore the plots for a range of neutral solutes will be super-imposable. In other words$\mathrm{ln\,(a_1)^{id}}$ is related to the ratio of amounts of solute to solvent. By adding a solute to a fixed amount of (solvent) water(λ) we lower the activity of water(λ) , (i.e. the chemical potential of water, μ(aq) in an aqueous solution) and stabilise the solvent.

The chemical potential of solute j in an aqueous solution $\mu_j(\mathrm{aq})$ is related to the molality of solute mj using equation (h) where $\mu_j^0(\mathrm{aq})$ is the chemical potential of solute j in an aqueous solution, molality $\mathrm{m_j} = 1\ \mathrm{mol\ kg^{-1}}$ and $\gamma_j = 1$ at all T and p, (taken as close to the standard pressure p^0).

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m^0}\right)$$

$$\mathrm{By\ definition,\ at\ all\ T\ and}\ p\,\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\gamma_\mathrm{j} \to 1$$

The role of water activity in determining enzyme activity is an important consideration [2]. .

Footnotes

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1.1.5: Activity of Solvents

Classically, the colligative properties of non-ionic solutions were used to determine the molar mass of solutes. For example, the depression $\Delta \mathrm{T}_f$ of the freezing point of water T_f at a given molalilty m_j of solute-j yields an estimate of the relative molar mass of the solute M_j. Key thermodynamic assumptions require that (a) on cooling only pure solvent separates out as the solid phase and (b) the thermodynamic properties of the solution are ideal. The key relationship emerges from the Schroder- van Laar equation [1]. The common assumption is that the thermodynamic properties of the solution are ideal. If the properties of a given aqueous solutions are determined to a significant extent by solute-solute interactions, a measured relative molar mass will be in error. Indeed McGlashan[2] was dismissive of the procedures based on Beckmann's apparatus for the determination of the relative molar mass of solute using freezing point measurements.

The chemical potential of water in an aqueous solution, $\mu_1(\mathrm{aq})$ at temperature T and pressure p (assumed to be close to the standard pressure, p^0) is related to the molality of solute j, m_j using equation (a) where R is the gas constant, ϕ is the practical osmotic coefficient and M_1 is the molar mass of water, $0.018015 \mathrm{kgmol}^{-1}$ where $\mu_1^*(\lambda)$ is the chemical potential of water(λ) at the same T and p.

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \phi \,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}$$

Chemical potential $\mu_1(\mathrm{aq})$ at temperature T is also related to $\mu_1^*(\lambda)$ using equation (b) where a_1 is the activity of water in the aqueous solution.

$$\mu_1\,(\mathrm{aq};\mathrm{m_j}) = \mu_1^*(\lambda) + \mathrm{R}\,\mathrm{T}\,\ln\,(\mathrm{a}_1)$$

Comparison of equations (a) and (b) shows that $\ln\,(a_1)$ is related to the molality of solute m_j using equation (c).

$$\ln\,(a_1) = -\phi\,\mathrm{M}_1\,\mathrm{m_j}$$

For a solution having thermodynamic properties which are ideal, the practical osmotic coefficient is unity.

$$\text{Then, } \ln\,(\mathrm{a}_1)^{\mathrm{id}} = -\mathrm{M}_1\,\mathrm{m_j}$$

Hence for a solution having thermodynamic properties which are ideal, $\ln\,(a_1)$ is a linear function of molality m_j, the plot having slope, $-(\mathrm{M}_1)$. Equation (d) forms a reference for a consideration of the properties of real solutions. For a solution having thermodynamic properties which are ideal, the solvent, water in an aqueous solution is at a lower chemical potential than the pure liquid. This observation is at the heart of the terms '**depression** of freezing point' and '**elevation** of boiling point'. In the event that the thermodynamic properties of a given solution are not ideal then the form of the plot showing $\ln\,(a_1)$ as a function of molality m_j is determined by ϕ which is, in turn, a function of m_j. The dependence of ϕ on m_j for a given solute in aqueous solutions (at fixed T and p) is not defined 'a priori'.

Bower and Robinson[3] report the dependence of osmotic coefficients for urea (aq) at 298 K over the range $0 \leq \mathrm{m_j}/\mathrm{molkg}^{-1} \leq 20.0$; ϕ decreases with increase in m_j. Similarly Stokes and Robinson [4] report the dependence of ϕ on solute molality for sucrose(aq), glucose(aq) and glycerol(aq) over the range $0 \leq \mathrm{m_j}/\mathrm{molkg}^{-1} \leq 7.5$.

For $\mathrm{m(\ urea\ )} = 8\ \mathrm{mol\ kg}^{-1}$, $\ln\,(a_1)$ equals -12×10^{-2} whereas $\ln\,(a_1)^{id}$ equals approx. -15×10^{-2}. At this molality for urea(aq), $\mu_1(\mathrm{aq}) > \mu_1(\mathrm{aq})^{\mathrm{id}}$ indicating that water in urea(aq) at this molality is at a higher chemical potential than would be the case for a solution where the thermodynamic properties are ideal. On the other hand for the hydrophilic solute sucrose where $\mathrm{m(\ sucrose\ )} = 6\ \mathrm{mol\ kg}^{-1}, \ln\,(\mathrm{a}_1)$ is -15×10^{-2} whereas $\ln\,(a_1)^{id}$ equals approx. -11×10^{-2} indicating that adding sucrose at this molality to water lowers the chemical potential of water relative to that for a solution having ideal properties.

For a dilute solution of simple neutral solutes the difference between ideal and real properties can be understood [5,6] in terms of the dependence of pairwise Gibbs energy interaction parameters g_{jj} on molality using equation (e) where $\mathrm{m}^0 = 1\ \mathrm{mol\ kg}^{-1}$; the units of g_{jj} are Jkg^{-1}.

$$1 - \phi = -(1/RT)\,g_{ij}\,\left(1/m^0\right)^2\,m_j$$

Using equation (c),

$$\ln(a_1) = -M_1\, m_j \left[1 + (RT)^{-1}\, g_{ij}\, \left(m^0\right)^{-2}\, m_j\right]$$

or

$$\ln(a_1) + M_1\, m_j = -M_1\, (RT)^{-1}\, g_{ij}\, \left(m^0\right)^{-2}\, (m_j)^2$$

Hence for dilute solutions $[\ln(a_1) + M_1\, m_j]$ is a linear function of $(\mathrm{m_j})^2$, the gradient of the plot yielding the pairwise Gibbs energy interaction parameter g_{jj}. If, for example, g_{jj} is positive indicating solute-solute repulsion, $[\ln(\mathrm{a_1}) + \mathrm{M_1\, m_j}]$ decreases with increase in m_j such that $\mu_1(\mathrm{aq}) > \mu_1(\mathrm{aq;id})$. In the event that solute-solute interactions are attractive, g_{jj} is negative. Hence the difference between the properties of real and ideal solutions is highlighted by the contrast between equations (d) and (f).

The analysis described above is readily extended to aqueous solutions containing two solutes; e.g. urea(aq) + sucrose(aq), [7] and glucose(aq) + sucrose(aq).[8]

Salt Solutions

A given aqueous salt solution contains a single salt j; μ1(aq) and μj(aq) are the chemical potentials of water and salt respectively in the closed system. For water,

$$\text{For water, } \mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \phi\, \mathrm{R\, T\, M_1\, v\, m_j}$$

$$\text{And } \mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \mathrm{R\, T\, \ln(a_1)}$$

Here ν is the stoichiometric parameter, the number of moles of ions produced by complete dissociation of one mole of salt j; for a 1:1 salt, ν equals 2. According to equations (h) and (i),

$$\ln(a_1) = -\phi\, M_1\, v\, m_j$$

$$\ln(a_1)^{\mathrm{id}} = -M_1\, v\, m_j$$

$$\text{If we confine attention to } 1:1 \text{ salts, } \ln(a_1)^{\mathrm{id}} = -2\, M_1\, m_j$$

With increase in m_j, $\ln(a_1)^{id}$ decreases linearly. With reference to equation (j), a) $\mathrm{limit}\,(\mathrm{m_j} \to 0)\, \phi = 1.0$. With dilution of a salt solution, a plot of ln(a1) against mj approaches a linear dependence.

$$\text{For the salt j, } \mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{v\, R\, T\, \ln\left(Q\, m_j\, \gamma_\pm / m^0\right)}$$

Here ν_+ and ν_- are the number of moles of cations and anions respectively produced by one mole of salt j; $v = v_+ + v_-; \gamma_\pm$ is the mean ionic activity γ coefficient of salt j. By definition, $\mathrm{Q^v = v_+^{v(+)}\, V_-^{v(-)}}$. Also $\mathrm{limit}\,(\mathrm{m_j} \to 0)\, \gamma_\pm = 1.0$ at all T and p; $\mu_\mathrm{j}^0(\mathrm{aq})$ is the chemical potential of salt j in a solution where $\mathrm{m_j} = 1\ \mathrm{mol\ kg^{-1}}$ and the thermodynamic properties of the solute are ideal; i.e. no ion-ion interactions.

For a 1:1 salt (e.g. KBr),

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + 2\, \mathrm{R\, T\, \ln\left(m_j\, \gamma_\pm / m^0\right)}$$

For a 1:1 salt where the thermodynamic properties of the solution are ideal,

$$\mu_j(\mathrm{aq;id}) = \mu_\mathrm{j}^0(\mathrm{aq}) + 2\, \mathrm{R\, T\, \ln\left(m_j / m^0\right)}$$

According to the Debye-Huckel Limiting Law, for very dilute solutions,

$$\ln(\gamma_\pm) = -S_\gamma\, \left(m_j / m^0\right)^{1/2}$$

where $S_\gamma = f(T, p, \varepsilon_r)$ and ε_r is the relative permittivity of the solvent at the same T and p.

$$\text{Further } [8, 9], 1 - \phi = (\mathrm{S_\gamma}/3)\, \left(\mathrm{m_j}/\mathrm{m^0}\right)^{1/2}$$

At 298.15 K and ambient pressure [8], $\mathrm{S_\gamma} = 0.5115$. In other words,

$$\phi^{\mathrm{dhll}} = 1 - (\mathrm{S_\gamma}/3)\, \left(\mathrm{m_j}/\mathrm{m^0}\right)^{1/2}$$

Hence using equation (j), for a 1:1 salt,

$$\ln\left(a_1\right)^{\mathrm{dhll}} + 2\,M_1\,m_j = \left[2\,\left(S_\gamma/3\right)\,M_1\,\left(m^0\right)^{-1/2}\right]\,\left(m_j\right)^{3/2}$$

Then $\ln\left(a_1\right)^{\mathrm{dhll}}$ indicates that for a salt solution, molality m_j, $\ln\left(a_1\right)$ exceeds that in the corresponding salt solution having ideal thermodynamic properties . In other words the activity of the solvent, water, is enhanced above that for water having ideal thermodynamic properties. For very dilute solutions $\left[\ln\left(a_1\right)^{\mathrm{dhll}} + 2\,M_1\,m_j\right]$ is a linear function of $\left(m_j\right)^{3/2}$. However other than for very dilute solutions equation (q) is inadequate and so a more sophisticated equation is required relating ϕ and m_j. Extensive compilations of ϕ for salt solutions are given in references [8] and [10].

Footnotes

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1.1.6: Activity of Solvents- Classic Analysis

Thermodynamics underpins a classic topic in physical chemistry concerning the depression of freezing point, ΔT_f of a liquid by added solute [1,2]. We note the superscript 'id' in equation (a) relating the activity of a solvent in an ideal solution, molality m_j.

$$\ln(a_1)^{id} = -M_1 m_j = -M_1 n_j/n_1^0 M_1 = -n_j/n_1^0$$

If the properties of a given aqueous solution are determined to a significant extent by solute-solute interactions, a determined molar mass for a given solute will be in error. Otherwise an observed depression is not a function of solute-solute interactions. Glasstone [2] comments that the ratio $\Delta T_f/m_j$ decreases with increasing concentration of solute, emphasising that a simple analysis is only valid for dilute solutions. Nevertheless the general idea is that the depression for a given mj is not a function of the hydration of a solute. Barrow [3] noted that the ratio $\Delta T_f/m_j$ for mannitol(aq) in very dilute solutions [4] is effectively constant. A similar opinion is advanced by Adam [5] who nevertheless comments on the importance of the condition 'dilute solution' in a determination of the molar mass of a given solute.

In summary, classic physical chemistry emphasises the importance of the superscript 'id' in equation (a). For very dilute solutions in a given solvent $\ln(a_1)$ is linear function of m_j, leading to description of such properties as 'depression of freezing point ' and 'elevation of boiling point ' under the heading 'colligative properties. Only the molality of solute mj is important; solute-solute interactions and hydration characteristics of solutes apparently play no part in determining these colligative properties.

The key to these statements is provided by the Gibbs-Duhem equation. For a solution prepared using 1 kg of water(λ) and m_j moles of a simple solute j, the Gibbs energy is given by equation (b).

$$G(aq) = (1/M_1)\ \mu_1(aq) + m_j\,\mu_j(aq)$$

Then, $G(aq) = (1/M_1)\ [\mu_1^*(\lambda) - \phi\,R\,T\,M_1\,m_j]$

$$+m_j\ \left[\mu_j^0\,(aq; id; m_j = 1) + R\,T\,\ln\left(m_j\,\gamma_j/m^0\right)\right]\ \ (c)$$

According to the Gibbs - Duhem Equation, the chemical potentials of solvent and solute are linked. At fixed T and p,

$$n_1\,d\mu_1(aq) + n_j\,d\mu_j(aq) = 0$$

Or, $(1/M_1)\ d\,[\mu_1^*(\lambda) - \phi\,R\,T\,M_1\,m_j]$

$$+m_j\,d\left[\mu_j^0\,(aq; id; m_j = 1) + R\,T\,\ln\left(m_j\,\gamma_j/m^0\right)\right] = 0$$

$$\text{Or,}\quad -d\,(\phi\,m_j) + m_j\,d\ln\left(m_j\,\gamma_j/m^0\right) = 0$$

$$\text{Or,}\quad -d\,(\phi\,m_j) + m_j\,d\ln\left(m_j\,\gamma_j/m^0\right) = 0$$

$$\text{Hence,}\quad (\phi - 1)\,\frac{dm_j}{m_j} + d\phi = d\ln(\gamma_j)$$

The latter equation forms the basis of the oft-quoted statement that if the thermodynamic properties of a solute are ideal then so are the properties of the solvent. Similarly if the thermodynamic properties of the solute are ideal then so are the properties of the solvent.

$$\text{From equation } (h), \phi = 1 + \frac{1}{m_j}\int_0^{m(j)} m_j\,d\ln(\gamma_j)$$

The importance of equation (i) emerges from the idea that γ_j describes the impact of solute-solute interactions on the properties of a given solution. If we can formulate an equation for $\ln(\gamma_j)$ in terms of the properties of the solution, we obtain ϕ from equation (i). If the properties of a real solution containing a neutral solute are not ideal, both γ_j and ϕ are linked functions of the solute molality. Pitzer [6] suggests equations (j) and (k) for $\ln(\gamma_j)$ and ϕ in terms of solute molalities using two parameters, λ and μ.

$$\ln(\gamma_j) = 2\,\lambda\,m_j + 3\,\mu\,(m_j)^2$$

$$\phi - 1 = \lambda\,m_j + 2\,\mu\,(m_j)^2$$

For example in the case of mannitol(aq) and butan-1-ol(aq), Pitzer [6] suggests the following equations for $\ln(\gamma_j)$.

$$\text{For mannitol(aq)} \quad \ln(\gamma_j) = -0.040\, m_j$$

$$\text{For butan-1-ol(aq)} \quad \ln(\gamma_j) = -0.38\, m_j + 0.51\, (m_j)^2$$

Guggenheim[7] using the mole fraction scale suggests equation (n) where A and B are characteristic of the solute.

$$1 - \phi = A\, x_j + B\, (x_j)^2$$

Prigogine and Defay [1] comment that the non-ideal properties of solutions can be understood in terms of the different molecular sizes of solute and solvent. A similar comment is made by Robinson and Stokes [8] who use a parameter describing the ratio of molar volumes of solute and solvent. The extent to which the properties of a solution differ from ideal can often be traced to a variety of causes including solvation, molecular size and shape.

Footnotes

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1.1.7: Activity of Water - Foods

An important scientific literature comments on the activity of water in the context of biochemistry and of the very important industry concerned with foods.[1-4]

Scott [5] identified the importance of water activity and microbial growth on foodstuffs; e.g. chilled beef. Hartel reviews the problem of freezing of water in, for example, ice cream; [6] see also comments on water activity in sucrose+ water systems.[1] The importance of water activity in sensory crispness and mechanical deformation of snack products is discussed by Katz and Labula. [7] Water activity is an important variable in fungal spoilage of food.[8,9]

Berg and Bruin review[10] the role of activity, not necessarily the water content, in the context of the deterioration of food, a matter of concern for humans from earliest times. In fact water activity, a1 is a major control variable in food preservation although the chemistry of food deterioration is complicated.

Crucially important in this context are publications produced by the National Institute of Standards and Technology .[11]

Footnotes

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1.1.8: Activity of Water - One Solute

Classical accounts of the physical chemical properties of solutions concentrate attention on the properties of solutes. Many experiments set out to determine activity coefficients γ_j for solutes in solution; (see also mean activity coefficients $\gamma_{\pm}$ for salts). Information concerning solvent activity is obtained by exploiting the Gibbs-Duhem equation which (at fixed T and p) links the properties of solute and solvent. However recent technological developments allow the activity of water in an aqueous solution to be measured [1].

The classic analysis of colligative properties of solutions by van't Hoff and others in the 19th Century is successful for dilute solutions. The importance of solute-solute interactions was generally recognised very early on in the 20th Century. However the role of solute-solvent interactions was perhaps underplayed.

We develop a model for a given solution prepared by dissolving n_j moles of neutral solute j, molar mass M_j, in ${n_1}^0$ moles of water(λ), molar mass M_1. The molality of solute **as prepared** is given by equation (a).

$$\mathrm{m_j(\ prepared\ ) = n_j/n_1^0\, M_1}$$

Then $\ln\left(a_1;\ \text{prepared}\right)^{\mathrm{id}}$ is given by equation (b).

\[\ln \left(a_{1}\right)^{i d}=-\(\mathrm{M}_{1} \, \(\mathrm{m}_{j}=-n_{j} / n_{1}^{0}]

However in another description of the solution under investigation each mole of solute j is strongly hydrated by h moles of water. The mass of solvent water, $\mathrm{w_1}$ is given by equation (c).

$$\mathrm{w_1 = \left[n_1^0 - h\, n_j\right]\ M_1}$$

Hence the molality of hydrated solute is given by equation (d).

\[\mathrm{m}_{\mathrm{j}}(\text { hydrated solute })=\mathrm{n}_{\mathrm{j}} /\left[\mathrm{n}_{1}^{0}-\mathrm{h} \, \mathrm{n}_{\mathrm{j}}\right] \, \mathrm{M}_{1}]

In effect the molality of the solute increases because there is less 'solvent water'

$$\text{By analogy with equation } (b), \ln\left(a_1;\ \text{hyd}\ \right) = -n_j/\left(n_1^0 - h\, n_j\right)$$

Therefore for a range of solutions containing different solutes but prepared using the same amount of solute, the activities are a function of the different extents of hydration of the solutes. With increase in h, $\ln\left(a_1;\ \text{hyd}\ \right)$ decreases (i.e. becomes more negative) indicative of increasing stabilisation of the water in the system by virtue of solute-water hydration interaction.

In a real solution, the properties of a solute are not ideal because there exist solute-solute communication by virtue of the fact that each solute molecule is 'aware' that some of the solvent has been 'removed' by solute hydration. The amount of solvent 'available ' to each molecule has been depleted by hydration of all solutes in solution. In other words a Gibbs-Duhem communication operates in the solution.

Hydration of Hydrophilic Solutes; Scatchard Model

The model of an aqueous solution described in conjunction with equation (a) is used to obtain the ratio, n_1^0/n_j; equation (f).

$$\text{Then, } \frac{n_1^0}{n_j} = \frac{1\ \mathrm{kg}}{M_1}\,\frac{M_j}{w_j}$$

Thus n_1^0/n_j describes the solution as prepared using n_j and ${n_1}^0$ moles of solutes and solvent respectively. We assert that by virtue of solute hydration an amount of water is removed from the 'solvent'. In solution the mole fraction of (solvent) water is x_1, the mole fraction of hydrated solute is x_j.

$$\text{Then,}\quad x_w + x_j = 1$$

The mole fraction ratio $\mathbf{X}_w/\mathbf{X}_j$ is given by equation (h).

\[\frac{\mathbf{X}_{w}}{X_{j}}=\frac{X_{w}}{1-X_{w}}]

Equation (h) forms the basis of a treatment described by Scatchard [2] in 1921, nearly a century ago. The model proposed by Scatchard [2] was based on a model for water(λ), described as a mixture of hydrols; monohydrols and polymerised water. Scatchard discusses hydration of solutes although not all solutes in a given solution are seen as hydrated; i.e. the solution contains various hydrates. In fact a given solute may be hydrated to varying degrees; i.e. a given solution contains various hydrates. However Scatchard envisaged [2] that one hydrate may be dominant. We note the date when the model was proposed by Scatchard [2]. The concept of hydrogen bonding in aqueous solutions has its origin in a paper published by Latimer and Roedbush in 1920 [3]; see also [4]; i.e. the previous year to publications by Scatchard [2].

Scatchard [2] invoked an assumption called the 'semi-ideal' assumption in which mole fraction \(x_{\mathrm{w}}\) in equation (h) is replaced by the activity of the solvent, water \(\mathrm{a}_{\mathrm{w}}\). Hence, from equation (h),

$$\text{Hence, from equation (h), } \frac{\mathrm{x_w}}{\mathrm{x_j}} = \frac{\mathrm{a_w}}{1-\mathrm{a_w}}$$

The difference between amounts of water defined by equations (f) and (i) yields the 'average degree of hydration', h of solute j.

$$\text{Then,} \quad \mathrm{h} = \frac{(1.0/0.0180)}{\mathrm{m_j}} - \frac{\mathrm{a_w}}{1-\mathrm{a_w}}$$

Equation (j) is Scatchard's equation. If one can measure \(\mathrm{a}_{\mathrm{w}}\) for an aqueous solution molality m_j we obtain the 'average degree of hydration' for solute j. Scatchard using vapour pressure data obtained an estimate of h for sucrose at 30 Celsius. In the case of a solution containing 34 g of sucrose in 100 g water(λ), h equals 4.46, decreasing with increase in the 'strength ' of the solution. The term 'semi-ideal' proposed by Scatchard emerges from the identification of solvent activity with mole fraction of depleted solvent. In summary Scatchard [2] obtained a property h but there is no indication of the stability of the hydrate.

Stokes and Robinson [5] extended the Scatchard analysis using a chemical equilibrium involving solute hydrates. The hydration of a given solute is described by a set of equilibrium constants describing i-hydration steps. For solute S,

$$\mathrm{S_{i-1} + H_2O \Leftrightarrows S_i} \quad (\mathrm{i} = 1, 2 \ldots \ldots \mathrm{n})$$

Each step is described by an equilibrium constant, K_i. So for a solute hydrated by 3 water molecules there are 3 equilibrium constants. Stokes and Robinson [5] set n equal to 11 for sucrose. However in this case Stokes and Robinson [5] simplify the analysis by assuming that the equilibrium constants for all hydration steps are equal. The resulting equations are as follows.

$$\frac{(1/\mathrm{M_1})}{\mathrm{m_j}} = \frac{\mathrm{a_w}}{1-\mathrm{a_w}} + \frac{\sigma}{\Sigma}$$

$$\text{where} \quad \sigma = \mathrm{K\,a_w} + \ldots\ldots\ldots + \mathrm{K\ (a_w)^n}$$

$$\text{and} \quad \Sigma = 1 + K\,a_w + \ldots\ldots\ldots + (K\,a_w)^n$$

Equation (λ) is interesting because for a given solute, the dependence of \(\mathrm{a}_{\mathrm{w}}\) on m_j yields two interesting parameters, n and K, describing hydration of a given solute j. The equilibrium constants defined above are dimensionless.

Stokes and Robinson [5] describe a method of data analysis but modern computer-based methods should lighten the arithmetic drudgery. For sucrose(aq) at 298.15 K Stokes and Robinson estimate that $n = 11$ and $\mathrm{K} = 0.994$. For glucose(aq) $n = 6$ with $\mathrm{K} = 0.786$. Finally we note that the composition of the solutions should be expressed in molalities; i.e. each solution made up by weight. If this is not done, conversion of concentrations to molalities is required. Possibly the literature will yield the required densities of the solutions. The worst approximation sets the density of the solutions at the density of water(λ) at the same temperature.

Footnotes

[1] Water Activity Meter, Decagon Devices Inc. WA 99163, USA.

[2] G. Scatchard, J.Am.Chem.Soc.,1921,**43**,2387.,2408.

[3] W. M. Latimer and W. H. Rodebush, J. Am. Chem.Soc.,1920,**42**,1419.

[4] L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, New York, 3rd edn.,1960, chapter 12.

[5] R. H. Stokes and R.A Robinson, J. Phys.Chem.,1966, **70**,2126.

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1.1.9: Activity of Water - Two Solutes

A given solution contains two neutral (i.e. non-ionic) solutes, solute-i and solute-j. We anticipate, for example, activity coefficient γ_i for solute $-i$ is a function of the molalities of both solutes, m_i and m_j. The thermodynamic properties of this class of solutions are discussed by Bower and Robinson [1] and by Ellerton and Dunlop [2]. Because the analysis discussed by these authors concerns the properties of solvent, water in aqueous solutions, the starting point is isopiestic vapour pressure measurements [1-3]. Analysis of the thermodynamic properties of these mixed aqueous solutions has four themes which we develop separately, drawing the analysis together in a final section.

Theme A

Solution I is prepared by dissolving ni moles of solute-i in water, mass $\mathrm{w}_1(\mathrm{I})$ at temperature T and pressure p(which is close to the standard pressure p^0); M_1 is the molar mass of water and $\phi(I)$ is the practical osmotic coefficient of the solvent, water, in solution(I). The contribution $\mathrm{G}_1(\mathrm{I})$ of the solvent to the Gibbs energy of the solution is given by equation(a).

$$\mathrm{G}_1(\mathrm{I}) = [\mathrm{w}_1(\mathrm{I})/\mathrm{M}_1]\ \{\mu_1^*(\lambda) - [\phi(\mathrm{I})\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_i}(\mathrm{I})]\}$$

Solution (II) is similarly prepared using n_j moles of solute-j in water, mass $\mathrm{w}_1(\mathrm{II})$.

$$\mathrm{G}_1(\mathrm{II}) = [\mathrm{w}_1(\mathrm{II})/\mathrm{M}_1]\ \{\mu_1^*(\lambda) - [\phi(\mathrm{II})\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}(\mathrm{II})]\}$$

We add a sample of solution (I) containing $1\ \mathrm{kg}$ of water to a sample of solution (II) also prepared using $1\ \mathrm{kg}$ of water. The resulting solution contains $2\ \mathrm{kg}$ of water and the initial molalities $\mathrm{m}_i(\mathrm{I})$ and $\mathrm{m}_j(\mathrm{II})$ will be reduced by a half. Then we imagine that $1\ \mathrm{kg}$ of water is withdrawn from the solution. This concentration process restores the original molalities of solutes i and j. The letter 'F' identifies the new solution.

$$\mathrm{G}_1(\ \mathrm{total}\ ; \mathrm{w}_1 = 1\ \mathrm{kg}) = (1/\mathrm{M}_1)\ \mu_1^*(\lambda) - \mathrm{R}\,\mathrm{T}\,\phi(\mathrm{F})\ [\mathrm{m_i}(\mathrm{I}) + \mathrm{m_j}(\mathrm{II})]$$

$\phi(\mathrm{F})$ is the practical osmotic coefficient of the solution prepared using solutions I and II from which $1\ \mathrm{kg}$ of solvent has been removed. The results of the analysis given above can be summarised in three equations describing the activities of water in the three solutions.

$$\ln[\mathrm{a}_1(\mathrm{I})] = -\phi(\mathrm{I})\,\mathrm{m_i}(\mathrm{I})\,\mathrm{M}_1$$

$$\ln[\mathrm{a}_1(\mathrm{II})] = -\phi(\ \mathrm{II}\ )\,\mathrm{m_j}(\mathrm{II})\,\mathrm{M}_1$$

$$\ln[\mathrm{a}_1(\ \mathrm{F})] = -\phi(\mathrm{F})\ [\mathrm{m_i}(\mathrm{I}) + \mathrm{m_j}(\mathrm{II})]\ \mathrm{M}_1$$

The molalities remain the same as in the original solutions; i.e. $\mathrm{m_i}(\mathrm{F}) = \mathrm{m_i}(\mathrm{I})$ and $\mathrm{m_j}(\mathrm{F}) = \mathrm{m_j}(\mathrm{II})$.

$$\text{By definition, } \Delta \equiv \phi(\mathrm{F})\ [\mathrm{m_i}(\mathrm{I}) + \mathrm{m_j}(\mathrm{II})] - [\phi(\mathrm{I})\,\mathrm{m_i}(\mathrm{I}) + \phi(\mathrm{II})\,\mathrm{m_j}(\mathrm{II})]$$

Experiments based on isopiestic measurements using the equilibrium between reference and mixed solutions and independently determined $\phi(\mathrm{I})$ and $\phi(\mathrm{II})$ yield the quantity Δ.

Theme B

The starting points are general equations for the activity coefficients γ_i and γ_j for solutes i and j respectively as a function of the molalities m_i and m_j in the mixed solutions. Two equations based on Taylor series are used.

$$\ln(\gamma_i) = \sum_{k=0}^{k=\infty}\sum_{\lambda=0}^{\lambda=\infty} A_{k\lambda}\ \left(m_i/m^0\right)^k\ \left(m_j/m^0\right)^\lambda$$

$$\ln(\gamma_k) = \sum_{k=0}^{k=\infty}\sum_{\lambda=0}^{\lambda=\infty} B_{k\lambda}\ \left(m_i/m^0\right)^k\ \left(m_j/m^0\right)^\lambda$$

With reference to equations (h) and (i), both A_{00} and B_{00} are zero. The dimensionless coefficients $\mathrm{A}_k\lambda$ and $\mathrm{B}_k\lambda$ are interlinked by the Gibbs-Duhem equation. It also turns out that the series up to and including '$k = 4$' and '$\lambda = 4$' are sufficient in the analysis of experimental results.

According to equation (h), a description of the properties of solute-i is given by equation (j).

$$\begin{aligned}\ln(\gamma_i) =& A_{10}\left(m_i/m^0\right) + A_{01}\left(m_j/m^0\right) + A_{20}\left(m_i/m^0\right)^2 \\ &+ A_{11}\left(m_i/m^0\right)\left(m_j/m^0\right) \\ &+ A_{02}\left(m_j/m^0\right)^2 + A_{30}\left(m_i/m^0\right)^3 + A_{21}\left(m_i/m^0\right)^2\left(m_j/m^0\right) \\ &+ A_{12}\left(m_i/m^0\right)\left(m_j/m^0\right)^2 + A_{03}\left(m_j/m^0\right)^3 + A_{40}\left(m_i/m^0\right)^4 \\ &+ A_{31}\left(m_i/m^0\right)^3\left(m_j/m^0\right) + A_{22}\left(m_i/m^0\right)^2\left(m_j/m^0\right)^2 \\ &+ A_{13}\left(m_i/m^0\right)\left(m_j/m^0\right)^3 + A_{04}\left(m_j/m^0\right)^4\end{aligned}$$

In the event that m_j is zero,

$$\begin{aligned}\ln\left[\gamma_i\left(m_j=0\right)\right] = & A_{10}\left(m_i/m^0\right) + A_{20}\left(m_i/m^0\right)^2 \\ &+ A_{30}\left(m_j/m^0\right)^3 + A_{40}\left(m_i/m^0\right)^4\end{aligned}$$

Moreover $\ln\left[\gamma_i\left(m_j=0\right)\right]$ can be calculated from the measured properties of aqueous solutions containing only solute-i. Therefore the dependence of $\ln\left[\gamma_i\left(m_j=0\right)\right]$ on m_i can be analysed using a linear least squares procedure to yield the coefficients A_{k0} for $k = 1 - 4$. Hence $\ln(\gamma_i)$ for the mixed solute system is given by a combination of equations (j) and (k) to yield equation (λ).

$$\begin{aligned}\ln(\gamma_i) = & \ln\left[\gamma_i\left(m_j=0\right)\right] \\ &+ A_{01}\left(m_j/m^0\right) + A_{11}\left(m_i/m^0\right)\left(m_j/m^0\right) + A_{02}\left(m_j/m^0\right)^2 \\ &+ A_{21}\left(m_i/m^0\right)^2\left(m_j/m^0\right) + A_{12}\left(m_i/m^0\right)\left(m_j/m^0\right)^2 \\ &+ A_{03}\left(m_j/m^0\right)^3 + A_{31}\left(m_i/m^0\right)^3\left(m_j/m^0\right) \\ &+ A_{22}\left(m_i/m^0\right)^2\left(m_j/m^0\right)^2 \\ &+ A_{13}\left(m_i/m^0\right)\left(m_j/m^0\right)^3 + A_{04}\left(m_j/m^0\right)^4\end{aligned}$$

According to equation (λ), the dependence of γ_i on m_j at fixed m_i is given by equation (m).

$$\begin{aligned}\left[\frac{\partial\ln(\gamma_i)}{\partial m_j}\right]_{m(i)} = & A_{01}\left(m^0\right)^{-1} + A_{11}\left(m_i/m^0\right)\left(m^0\right)^{-1} + A_{02}\,2\,m_j\left(m^0\right)^{-2} \\ &+ A_{21}\left(m_i/m^0\right)^2\left(m^0\right)^{-1} + A_{12}\left(m_i/m^0\right)2\,m_j\left(m^0\right)^{-2} \\ &+ A_{03}\,3\left(m_j\right)^2\left(m^0\right)^{-3} + A_{31}\left(m_i/m^0\right)^3\left(m^0\right)^{-1} \\ &+ A_{22}\left(m_i/m^0\right)^2 2\,m_j\left(m^0\right)^{-2} + A_{13}\left(m_i/m^0\right)3\left(m_j\right)^2\left(m^0\right)^{-3} \\ &+ A_{04}\,4\left(m_j\right)^3\left(m^0\right)^{-4}\end{aligned}$$

A cross-differential link yields the following interesting equation.

$$\left[\frac{\partial\ln(\gamma_i)}{\partial m_j}\right]_{m(i)} = \left[\frac{\partial\ln(\gamma_j)}{\partial m_i}\right]_{m(j)}$$

We combine equations (m) and (n).

$$\begin{aligned}\left[\frac{\partial\ln(\gamma_j)}{\partial m_i}\right]_{m(j)} = & A_{01}\left(m^0\right)^{-1} + A_{11}\left(m_i/m^0\right)\left(m^0\right)^{-1} + A_{02}\,2\,m_j\left(m^0\right)^{-2} \\ &+ A_{21}\left(m_i/m^0\right)^2\left(m^0\right)^{-1} + A_{12}\left(m_i/m^0\right)2\,m_j\left(m^0\right)^{-2} \\ &+ A_{03}\,3\left(m_j\right)^2\left(m^0\right)^{-3} + A_{31}\left(m_i/m^0\right)^3\left(m^0\right)^{-1} \\ &+ A_{22}\left(m_i/m^0\right)^2 2\,m_j\left(m^0\right)^{-2} + A_{13}\left(m_i/m^0\right)3\left(m_j\right)^2\left(m^0\right)^{-3} \\ &+ A_{04}\,4\left(m_j\right)^3\left(m^0\right)^{-4}\end{aligned}$$

We integrate the latter equation to yield an equation for $\gamma_j\left(m_i=0\right)$ where at '$m_i = 0$', γ_j is represented as $\gamma_j(\,m_i = 0)$. The outcome is an equation for $\ln(\gamma_j)$ in terms of the A_i-variables, making the B_i variables somewhat redundant.

$$\begin{aligned}\ln(\gamma_j) =& \ln[\gamma_j(m_i=0)] \\ &+A_{01}(m_i/m^0)+(A_{11}/2)(m_i/m^0)^2+2A_{02}(m_i m_j)(m^0)^{-2} \\ &+(A_{21}/3)(m_i/m^0)^3+A_{12}(m_i/m^0)^2 m_j (m^0)^{-1} \\ &+3A_{03} m_i (m_j)^2 (m^0)^{-3} \\ &+(1/4)A_{31}(m_i/m^0)^4 \\ &+(2A_{22}/3)(m_i)^3 m_j (m^0)^{-4}+(3A_{13}/2)(m_i)^2 (m_j)^2 (m^0)^{-4} \\ &+4A_{04} m_i (m_j)^3 (m^0)^{-4}\end{aligned}$$

Theme C Gibbs-Duhem Equations

A Single Solute

For an aqueous solution at fixed T and p containing the single solute-i, the Gibbs-Duhem equation yields the following relationship.

$$n_1\, d\mu_1(aq) + n_i\, d\mu_i(aq) = 0$$

$$\text{Then, } \frac{1}{M_1} d[\mu_1^*(\lambda) - \phi_i R T M_1 m_i] + m_i\, d\left[\mu_i^0(aq) + R T \ln\left(m_i \gamma_i / m^0\right)\right] = 0$$

The symbol ϕ_i identifies the practical osmotic coefficient in a solution containing solute-i.

$$\text{Hence [4]}, \quad d[\phi_i m_i] = dm m_i + m_i\, d\ln(\gamma_i)$$

Similarly for an aqueous solutions containing solute-j,

$$d[\phi_j m_j] = dm m_j + m_j\, d\ln(\gamma_j)$$

Two Solutes

From the Gibbs-Duhem equation (at fixed T and p)

$$n_1\, d\mu_1(aq) + n_i\, d\mu_i(aq) + n_j\, d\mu_j(aq) = 0$$

Then,

$$\begin{aligned}&\frac{1}{M_1} d[\mu_1^*(\lambda) - \phi_{ij} R T M_1 (m_i + m_j)] \\ &+m_i\, d\left[\mu_i^0(aq) + R T \ln\left(m_i \gamma_i / m^0\right)\right] \\ &+m_j\, d\left[\mu_j^0(aq) + R T \ln\left(m_j \gamma_j / m^0\right)\right] = 0\end{aligned}$$

The practical osmotic coefficient ϕ_{ij} identifies a solution containing two solutes, i and j.

$$\text{Hence, } d[\phi_{ij}(m_i + m_j)] = m_j\, d\ln\left(m_j \gamma_j / m^0\right) + m_i\, d\ln\left(m_i \gamma_i / m^0\right)$$

$$\text{Therefore[5] } d[\phi_{ij}(m_i + m_j)] = d(m_i + m_j) + m_i\, d\ln(\gamma_j) + m_j\, d\ln(\gamma_j)$$

According to equation (g)

$$\Delta \equiv \phi(F)[m_i(I) + m_j(II)] - [\phi(I) m_i(I) + \phi(II) m_j(II)]$$

$$\text{Then } d\Delta = d\{\phi(F)[m_i(I) + m_j(II)]\} - d[\phi(I) m_i(I)] - d[\phi(II) m_j(II)]$$

Labels (I) and (II) can be dropped when applied to solute molalities. Then using equations (s), (t) and (x),

$$\begin{aligned}d\Delta =& d(m_i + m_j) + m_i\, d\ln[\gamma_i(F)] + m_j\, d\ln[\gamma_j(F)] \\ &-dm_i - m_i\, d\ln[\gamma_i(I)] - dm_j - m_j\, d\ln[\gamma_j[II]\end{aligned}$$

$$\text{Or, } d\Delta = m_i\, d\{\ln(\gamma_i(F) - \ln[\gamma_j(I)]\} + m_j\, d\{\ln[\gamma_j(F)] - d\ln[\gamma_j[II]\}$$

In equation (λ) we identify $\ln[\gamma_i(m_j = 0)]$ with $\ln[\gamma_i(I)]$. Similarly $\ln[\gamma_j(m_i = 0)]$ in equation (p) equals $\ln[\gamma_j(II)]$ in equation (za). Therefore [6]

$$\begin{aligned}
&\Delta/m_i\, m_j\, \left(m^0\right)^{-1} \\
&= A_{01} + A_{11}\, m_i\, \left(m^0\right)^{-1} + 2\, A_{02}\, m_j\, \left(m^0\right)^{-1} + A_{21}\, \left(m_i\right)^2\, \left(m^0\right)^{-2} \\
&\quad + (3/2)\, A_{12}\, m_i\, m_j\, \left(m^0\right)^{-2} + 3\, A_{03}\, \left(m_j\right)^2\, \left(m^0\right)^{-2} + A_{31}\, \left(m_i/m^0\right)^3 \\
&\quad + (4/3)\, A_{22}\, \left(m_i\right)^2\, m_j\, \left(m^0\right)^{-3} + 2\, A_{13}\, m_i\, \left(m_j\right)^2\, \left(m^0\right)^{-3} \\
&\quad + 4\, A_{04}\, \left(m_j\right)^3\, \left(m^0\right)^{-3}
\end{aligned}$$

Footnotes

[1] V. E. Bower and R. A. Robinson , J.Phys.Chem.,1963,**67**,1524.

[2] H. D. Ellerton and P. J. Dunlop, J. Phys Chem.1966,**70**,1831.

[3] H. D. Ellerton, G. Reinfelds, D. E. Mulcahy and P. J. Dunlop, J. Phys. Chem., 1964, **68**,398.

[4] Hence, $-\mathrm{d}\left[\phi_i\, m_i\right] + m_i\, \mathrm{d}\ln\left(m_i\, \gamma_i/m^0\right) = 0$

Then, $-\mathrm{d}\left[\phi_i\, m_i\right] + m_i\, \mathrm{d}\left[\ln\left(m_i\right) + \ln\left(\gamma_i\right) - \ln\left(m^0\right)\right] = 0$

Or, $\mathrm{d}\left[\phi_i\, m_i\right] = m_i\, \frac{1}{m_i}\mathrm{d}mm_i + m_i\, \mathrm{d}\ln\left(\gamma_i\right)$

Then, $\mathrm{d}\left[\phi_i\, m_i\right] = \mathrm{d}m_i + m_i\, \mathrm{d}\ln\left(\gamma_i\right)$

[5] Or,

$$\begin{aligned}
&\mathrm{d}\left[\phi_{ij}\, \left(m_i + m_j\right)\right] \\
&\quad = m_j\, \mathrm{d}\ln\left(m_j/m^0\right) + m_j\, \mathrm{d}\ln\left(\gamma_j\right) + m_i\, \mathrm{d}\ln\left(m_i/m^0\right) + m_j\, \mathrm{d}\ln\left(\gamma_j\right)
\end{aligned}$$

Or

$$\begin{aligned}
&\mathrm{d}\left[\phi_{ij}\, \left(m_i + m_j\right)\right] \\
&\quad = \left(m_j/m_j\right)\, \mathrm{d}\left(m_j/m^0\right) + m_j\, \mathrm{d}\ln\left(\gamma_j\right) + \left(m_i/m_i\right)\, \mathrm{d}\left(m_i/m^0\right) + m_j\, \mathrm{d}\ln\left(\gamma_j\right)
\end{aligned}$$

Or,

$$\begin{aligned}
&\mathrm{d}\left[\phi_{ij}\, \left(m_i + m_j\right)\right] \\
&\quad = \mathrm{d}\left(m_j + m_i\right) + m_i\, \mathrm{d}\ln\left(\gamma_i\right) + m_j\, \mathrm{d}\ln\left(\gamma_j\right)
\end{aligned}$$

[6] Differentiation of equation (λ) yields

$$\begin{aligned}
&\mathrm{d}\left\{\ln\left[\gamma_i(\mathrm{F})\right] - \ln\left[\gamma_i(\mathrm{I})\right]\right\} = \\
&A_{01}\, \left(m^0\right)^{-1}\, \mathrm{d}m_j + A_{11}\, m_j\, \left(m^0\right)^{-2}\, \mathrm{d}m_i + A_{11}\, m_i\, \left(m^0\right)^{-2}\, \mathrm{d}m_j \\
&+ 2\, A_{02}\, m_j\, \left(m^0\right)^{-2}\, \mathrm{d}m_j + 2\, A_{21}\, m_i\, m_j\, \left(m^0\right)^{-3}\, \mathrm{d}m_i \\
&+ A_{21}\, \left(m_i\right)^2\, \left(m^0\right)^{-3}\, \mathrm{d}mm_j + A_{12}\, \left(m_j\right)^2\, \left(m^0\right)^{-3}\, \mathrm{d}m_i \\
&+ 2\, A_{12}\, m_i\, m_j\, \left(m^0\right)^{-3}\, \mathrm{d}mj_j + 3\, A_{03}\, \left(m_j\right)^2\, \left(m^0\right)^{-3}\, \mathrm{d}mm_j \\
&+ 3\, A_{31}\, \left(m_i\right)^2\, m_j\, \left(m^0\right)^{-4}\, \mathrm{d}m_i + A_{31}\, \left(m_i\right)^3\, \left(m^0\right)^{-4}\, \mathrm{d}m_j \\
&+ 2\, A_{22}\, m_i\, \left(m_j\right)^2\, \left(m^0\right)^{-4}\, \mathrm{d}m_i + 2\, A_{22}\, \left(m_i\right)^2\, m_j\, \left(m^0\right)^{-4}\, \mathrm{d}m_j \\
&+ A_{13}\, \left(m_j\right)^3\, \left(m^0\right)^{-4}\, \mathrm{d}m_i + 3\, A_{13}\, m_i\, \left(m_j\right)^2\, \left(m^0\right)^{-4}\, \mathrm{d}m_j \\
&+ 4\, A_{04}\, \left(m_j\right)^3\, \left(m^0\right)^{-4}\, \mathrm{d}m_j
\end{aligned}$$

Similarly from equation (p),

$$
\begin{aligned}
&\mathrm{d}\left\{\ln\left[\gamma_j(\mathrm{F})\right]-\ln\left[\gamma_j(\mathrm{I})\right]\right\}= \\
&\mathrm{A}_{01}\ \left(\mathrm{m}^0\right)^{-1}\ \mathrm{dm_i}+\mathrm{A}_{11}\,\mathrm{m_i}\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{dm_i} \\
&+2\,\mathrm{A}_{02}\,\mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{dm_i}+2\,\mathrm{A}_{02}\,\mathrm{m_i}\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{dm_j} \\
&+\mathrm{A}_{21}\ \left(\mathrm{m_i}\right)^2\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_i}+2\,\mathrm{A}_{12}\,\mathrm{m_i}\,\mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_i} \\
&+\mathrm{A}_{12}\ \left(\mathrm{m_i}\right)^2\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dmm_j}+3\,\mathrm{A}_{03}\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_i} \\
&+6\,\mathrm{A}_{03}\,\mathrm{m_i}\,\mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_j}+\mathrm{A}_{31}\ \left(\mathrm{m_i}\right)^3\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_i} \\
&+\mathrm{A}_{22}\ \left(\mathrm{m_i}\right)^2\ \mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dmm_i}+(2/3)\,\mathrm{A}_{22}\ \left(\mathrm{m_i}\right)^3\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm} \\
&\mathrm{j} \\
&+3\,\mathrm{A}_{13}\,\mathrm{m_i}\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_i} \\
&+3\,\mathrm{A}_{13}\ \left(\mathrm{m_i}\right)^2\ \mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_j}+4\,\mathrm{A}_{04}\ \left(\mathrm{m_j}\right)^3\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_i} \\
&+12\,\mathrm{A}_{04}\,\mathrm{m_i}\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_j}
\end{aligned}
$$

But according to equation (za),

$$
\mathrm{d}\Delta=\mathrm{m_i}\,\mathrm{d}\left\{\ln\left(\gamma_i(\mathrm{F})-\ln\left[\gamma_j(\mathrm{I})\right]\right\}+\mathrm{m_j}\,\mathrm{d}\left\{\ln\left[\gamma_j(\mathrm{F})\right]-\mathrm{d}\ln\left[\gamma_j[\mathrm{II}]\right\}\right.
$$

After rearranging one obtains the following equation.

$$
\begin{aligned}
&\mathrm{d}\Delta= \\
&\mathrm{A}_{01}\,\mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-1}\ \mathrm{dm_i}+\mathrm{A}_{01}\,\mathrm{m_i}\ \left(\mathrm{m}^0\right)^{-1}\ \mathrm{dm_j} \\
&+2\,\mathrm{A}_{11}\,\mathrm{m_i}\,\mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{dm_i}+\mathrm{A}_{11}\ \left(\mathrm{m_i}\right)^2\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{dm_j} \\
&+2\,\mathrm{A}_{02}\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{dm_i}+4\,\mathrm{A}_{02}\,\mathrm{m_i}\,\mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{dm_j} \\
&+3\,\mathrm{A}_{21}\ \left(\mathrm{m_i}\right)^2\ \mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_i}+\mathrm{A}_{21}\ \left(\mathrm{m_i}\right)^3\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_j} \\
&+3\,\mathrm{A}_{12}\,\mathrm{m_i}\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_i}+3\,\mathrm{A}_{12}\ \left(\mathrm{m_i}\right)^2\ \mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_j} \\
&+3\,\mathrm{A}_{03}\ \left(\mathrm{m_j}\right)^3\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_i}+9\,\mathrm{A}_{03}\,\mathrm{m_i}\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-3}\ \mathrm{dm_j} \\
&+4\,\mathrm{A}_{31}\ \left(\mathrm{m_i}\right)^3\ \mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_i}+\mathrm{A}_{31}\ \left(\mathrm{m_i}\right)^4\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_j} \\
&+4\,\mathrm{A}_{22}\ \left(\mathrm{m_i}\right)^2\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_i}+(8/3)\,\mathrm{A}_{22}\ \left(\mathrm{m_i}\right)^3\ \mathrm{m_j}\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_j} \\
&+4\,\mathrm{A}_{13}\,\mathrm{m_i}\ \left(\mathrm{m_j}\right)^3\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_i}+6\,\mathrm{A}_{13}\ \left(\mathrm{m_i}\right)^2\ \left(\mathrm{m_j}\right)^2\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_j} \\
&+4\,\mathrm{A}_{04}\ \left(\mathrm{m_j}\right)^4\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_i}+16\,\mathrm{A}_{04}\,\mathrm{m_i}\ \left(\mathrm{m_j}\right)^3\ \left(\mathrm{m}^0\right)^{-4}\ \mathrm{dm_j}
\end{aligned}
$$

Term by term integration of the latter equation yields

$$
\Delta=\int\mathrm{d}\Delta
$$

As an example we cite the terms containing the coefficient A_{11}.

$$
\begin{aligned}
&\int 2\,A_{11}\,m_i\,m_j\ \left(m^0\right)^{-2}\ dm_i+\int A_{11}\ \left(m_i\right)^2\ \left(m^0\right)^{-2}\ dm_j \\
&=A_{11}\ \left(m^0\right)^{-2}\ dm_i\int\left[2\,m_i\,m_j\,dm_i+\left(m_i\right)^2\ dm_j\right] \\
&=A_{11}\ \left(m^0\right)^{-2}\int d\left[\left(m_i\right)^2\ m_j\right] \\
&=A_{11}\ \left(m^0\right)^{-2}\ \left(m_i\right)^2\ m_j
\end{aligned}
$$

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1.1.10: Activity Coefficient- Two Neutral Solutes- Solute + Trace Solute i

A given solution is prepared using n1 moles of water(λ) together with n_i and n_j moles of neutral solutes i and j respectively at temperature T and pressure p (which is close to the standard pressure p^0). The mass of water is $\mathrm{n_1\,M_1}$ where $\mathrm{M_1}$ is the molar mass of water. Hence the molalities of solutes i and j are $\mathrm{m_i\,(=n_i/n_1\,M_1)}$ and $\mathrm{m_j\,(=n_j/n_1\,M_1)}$ respectively. The chemical potential of water in the aqueous solution $\mu_1(\mathrm{aq})$ is related to the molality of solutes using equation (a) where ϕ is the practical osmotic coefficient and $\mu_1^*(\lambda)$ is the chemical potential water(λ) at the same T and p.

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \phi\,\mathrm{R\,T\,M_1\ (m_i + m_j)}$$

The chemical potentials of the two solutes, $\mu_\mathrm{i}(\mathrm{aq})$ and $\mu_\mathrm{j}(\mathrm{aq})$, are related to m_i and m_j together with corresponding activity coefficients, γ_i and γ_j using equations (b) and (c).

$$\mu_\mathrm{i}(\mathrm{aq}) = \mu_\mathrm{i}^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_i\,\gamma_i/m^0\right)}$$

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_j\,\gamma_j/m^0\right)}$$

Here $\mu_i^0(\mathrm{aq})$ is the reference chemical potential for solute i in a solution where $\mathrm{m_j = 0\ mol\ kg^{-1}}$, $\mathrm{m_i = 1\ mol\ kg}$ and $\gamma_i = 1$. A similar definition operates for solute j. For the mixed solution at all T and p,

$$\mathrm{limit\,(m_i \to 0; m_j \to 0)}\,\gamma_\mathrm{i} = 1$$

$$\mathrm{limit\,(m_i \to 0; m_j \to 0)}\,\gamma_\mathrm{j} = 1$$

In these terms, the thermodynamic properties of solute i are not ideal as a consequence of $i-i$, $j-j$ and $i-j$ solute-solute interactions. A similar comment concerns the thermodynamic properties of solute j. With increase in molalities m_i and m_j, so the extent to which the thermodynamic properties deviate from ideal increases; i.e. for solute j, $\gamma_j \neq 1$ and for solute i, $\gamma i \neq 1$. Such deviations can be understood in terms of $i-i$, $j-j$, and $i-j$ solute-solute interactions.

In some applications of this analysis, solute i is present in trace amounts and so γ_i in the absence of solute j would be close to unity. However as the molality of solute j is increased, the thermodynamic properties of solute i deviate increasingly from ideal as a result of solute $i \rightleftarrows$ solute j interactions. This feature can be described [1,2] quantitatively using equation (f) where $\beta_1, \beta_2 \ldots$ describe the role of pairwise i-j , triplet $i-j-j \ldots\ldots$ solute-solute interactions.

$$\ln(\gamma_i) = \beta_1\,\left(m_j/m^0\right) + \beta_2\,\left(m_j/m^0\right)^2 + \ldots\ldots$$

Depending on the signs of the β - coefficients , added solute j can either stabilise or destabilise solute-i; i.e. either lower or raise $\mu_i(aq)$ relative to that in a solution having ideal thermodynamic properties.

Footnotes

[1] Based on an analysis suggested by C. Wagner, Thermodynamics of Alloys, Addison-Wesley, Reading, Mass., 1952, pages 19-22.

[2] As quoted by G. N. Lewis and M. Randall, Thermodynamics, 2nd edn., revised by K. S. Pitzer and L Brewer, McGraw-Hill, New York, 1961, page 562.

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1.1.11: Activity Coefficients

In descriptions of the properties of the components of liquid mixtures, rational activity coefficients are given the symbols $f_1, f_2, f_3 \ldots$. With reference to solvents their thermodynamic properties are described by rational activity coefficients $f_1, f_2, f_3 \ldots$ and (practical) osmotic coefficient, ϕ. The properties of solutes in solutions are described using activity coefficients which are linked to the descriptions of the composition of solutions: molality scale, γ_j; concentration scale γ_j; mole fraction scale f_j^*.

These coefficients are intimately related to the concept of **activity**. Their significance is clarified by equations relating chemical potentials to the composition of a given system; e.g.

i. components in liquid mixtures,
ii. solvents in solutions and
iii. solutes in solutions.

In all cases they summarise the extent to which the thermodynamic properties of liquid mixtures and solutions are not ideal. The challenge for chemists is to understand in terms of molecular properties why the thermodynamic properties of real systems are not ideal. It has to be admitted that activity coefficients have a 'bad press' as far as most chemists are concerned. All too often their importance is ignored. But 'learn to love activity coefficients! Perhaps the importance of activity coefficients can be understood in the following terms.

The chemical potential of urea as a solute in aqueous solutions, $\mu_j(\mathrm{aq})$ at temperature T and pressure p ($\approx$ the standard pressure p^0) is related to the molality of urea m_j using equation (a).

$$\mu_j(\mathrm{aq};\mathrm{T},\mathrm{p}) = \\ \mu_j^0\left(\mathrm{aq};\mathrm{T},\mathrm{p},\mathrm{m_j}=1\ \mathrm{mol\ kg\ kg^{-1}}\right)+\mathrm{R\,T\ ln}\left(\mathrm{m_j}/\mathrm{m}^0\right)+\mathrm{R\,T\ ln}\left(\gamma_j\right)$$

The term $\mu_j^0\left(\mathrm{aq};\mathrm{T},\mathrm{p},\mathrm{m_j}=1\ \mathrm{molkg}^{-1}\right)$ describes the chemical potential of solute, urea in an aqueous solution having unit molality where there are no urea - urea (i.e. solute – solute) interactions. Each urea molecule in these terms is unaware of the presence of other urea molecules in the aqueous solution. In a solution having ideal thermodynamic properties $\mu_j(\mathrm{aq};\mathrm{T},\mathrm{p};\mathrm{id})$ depends on the molality of solute mj. Thus the osmotic pressure of this solution is a function of the molality of urea. For such an ideal solution there are no urea-urea interactions although there are important urea-water interactions, the hydration of urea. But in a real solution there are also solute-solute interactions. Each solute molecule 'knows' there are other solute molecules in the solution. Indeed the extent to which $\mu_j(\mathrm{aq};\mathrm{T},\mathrm{p})$ differs from $\mu_j(\mathrm{aq};\mathrm{T},\mathrm{p};\mathrm{id})$ is a function of the molality of the solute, m_j.

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1.1.12: Activity Coefficients- Salt Solutions- Ion-Ion Interactions

For most dilute aqueous salt solutions (at ambient temperature and pressure), mean ionic activity coefficients γ± are less than unity. Thus ion-ion interactions within a real solution lower chemical potentials below those of salts in the corresponding ideal solutions. Clearly a quantitative treatment of this stabilisation is enormously important. In fact for almost the whole of the 20th Century, scientists offered theoretical bases for expressing $\ln(\gamma_{\pm})$ as a function of the composition of a salt solution, temperature, pressure and electric permittivity of the solvent.

In effect we offer as much information as demanded by the theory (e.g. molality of salt, nature of salt, permittivity of solvent, ion sizes, temperature, pressure, ...). We set the apparently simple task - please calculate the mean activity coefficient of the salt in this solution.

Many models and treatments have been proposed [1]. Most models start by considering a reference j-ion in an aqueous salt solution. In order to calculate the electric potential at the j-ion arising from all other ions in solution, we need to know the distribution of these ions about the j-ion. Unfortunately this distribution is unknown and so we need a model for this distribution. Further activity coefficients reflect the impact of ions on water-water interactions in aqueous solutions [2] .

Footnotes

[1] (a) R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd. edition revised,1965. (b) H. S. Harned and B. B. Owen., The Physical Chemistry of Electrolytic Solutions ,Reinhold, New York, 2nd. edn.,1950, chapter The analysis presented by Harned and Owen anticipates application to irreversible processes; e.g. electric conductance of salt solutions. Here we confine attention to equilibrium properties.

[2] H. S. Frank, Z. Phys. Chem., 1965,228,364.

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1.1.13: Activity of Water - Salt Solutions

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SECTION OVERVIEW

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1.2.1: Affinity for Spontaneous Chemical Reaction

A given closed system is prepared using ethyl ethanoate(aq) in an alkaline solution. The composition of the system changes spontaneously as a consequence of chemical reaction. The latter is described by the following chemical equation.

$$CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$$

At each stage, the **extent of chemical reaction** is represented by the symbol ξ. The composition of the system varies with time as the reaction proceeds. At any given instant we characterise the rate of chemical reaction by $\mathrm{d}\xi/\mathrm{dt}$. We also ask 'why did chemical reaction proceed in this direction?' The answer is − the chemical reaction is driven in that direction by the affinity for spontaneous change, symbol A [1-3]. The affinity A for spontaneous chemical reaction is defined by the second law of thermodynamics which states that,

$$\mathrm{T\,dS} = \mathrm{q} + \mathrm{A\,d}\xi$$

$$\text{where } A\,d\xi \geq 0$$

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1.2.2: Affinity for Spontaneous Reaction- Chemical Potentials

For a closed system containing $\mathrm{k}-$ chemical substances, the differential dependence of Gibbs energy on temperature, pressure and chemical composition, is given by the following equation.

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} + \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{k}} \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}} \mathrm{dnj_j}$$

The condition at constant $n(i \neq j)$ indicates that the amounts of each i chemical substance except chemical substance j is constant. The Gibbs energy of a closed system is a thermodynamic potential function; equation (b).

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} - \mathrm{A}\,\mathrm{d}\xi$$

Here A is the affinity for spontaneous chemical reaction producing a change in extent of reaction, $\mathrm{d}\xi$, in this case a change in composition. Further the chemical potential of chemical substance j,

$$\mu_{\mathrm{j}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}}$$

Comparison of equations (a) and (b) yields equation(d).

$$-A\,d\xi = \sum_{j=1}^{j=k} \mu_j\,dn_j$$

The stoichiometry in a chemical reaction for chemical substance j, ν_j is defined such that ν_j is positive for products and negative for reactants; a mnemonic is ‘P for P’.

$$v_j = dn_j/d\xi$$

Hence the affinity for spontaneous change,

$$A = -\sum_{j=1}^{j=k} v_j\,\mu_j$$

But at equilibrium, the affinity for spontaneous change A is zero.

$$\text{Then, } \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{k}} \mathrm{v_j}\,\mu_{\mathrm{j}}^{\mathrm{eq}} = 0$$

Equation (g) in terms of its simplicity is misleading. Chemists are experts at assaying a system at equilibrium in order to determine the chemical substances present and their amounts. For example, an assay of a given system yields (for defined temperature and pressure) the amounts of un-dissociated acid $\mathrm{CH_3COOH(aq)}$, and the conjugate base $\mathrm{CH_3COO^-(aq)}$ and hydrogen ions at equilibrium. We write equation (g) as follows.

$$-\mu^{\mathrm{eq}}\left(\mathrm{CH_3COOH;aq}\right) + \mu^{\mathrm{eq}}\left(\mathrm{CH_3COO^-;aq}\right) + \mu^{\mathrm{eq}}\left(\mathrm{H^+;aq}\right) = 0$$

Or, representing a balance of chemical potentials, (a useful approach)

$$\mu^{\mathrm{eq}}\left(\mathrm{CH_3COOH;aq}\right) = \mu^{\mathrm{eq}}\left(\mathrm{CH_3COO^-;aq}\right) + \mu^{\mathrm{eq}}\left(\mathrm{H^+;aq}\right)$$

The concept of a balance of equilibrium chemical potentials at thermodynamic equilibrium is often the starting point for a description of the properties of closed systems.

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1.2.3: Affinity for Spontaneous Chemical Reaction- Phase Equilibria

A given system comprises two phases, I and II, both phases comprising i-chemical substances. We consider the transfer of one mole of chemical substance j from phase I to phase II. The affinity for the transfer is given by equation (a).

$$\mathrm{A_j} = \mu_\mathrm{j}(\mathrm{I}) - \mu_\mathrm{j}(\mathrm{II})$$

If $\mu_j(\mathrm{II}) < \mu_\mathrm{j}(\mathrm{I})$, A_j is positive and the process is spontaneous. If the system is at fixed T and pressure, the gradient of Gibbs energy is negative [1].

$$\mathrm{A_j} = -(\partial \mathrm{G}/\partial\xi)_{\mathrm{T,p}} = \mu_j(\mathrm{I}) - \mu_\mathrm{j}(\mathrm{II})$$

We suppose the mole fraction of substance –j in phases I and II are $x_j(\mathrm{I})$ and $x_j(\mathrm{II})$. We express the chemical potentials as functions of the mole fraction compositions of the two phases.

$$\begin{aligned} A_j = \mu_j^*(I) + RT\,\ln\left[x_j(I)\,f_j(I)\right] \\ - \mu_j^*(II) - RT\,\ln\left[x_j(II)\,f_j(II)\right] \end{aligned}$$

Here $\mathrm{f}_j(\mathrm{I})$ and $\mathrm{f}_j(\mathrm{II})$ are rational activity coefficients of substance j in phases I and II respectively.

$$\text{At all } T \text{ and p, both } \lim\left(x_j(I) \to 1\right) f_j(I) = 1$$

$$\text{and } \lim\left(\mathrm{x_j\ (II)}\ \to 1\right) \mathrm{f_j(\ II\ )} = 1$$

$$\text{By definition } \mu_j^*(\mathrm{II}) - \mu_\mathrm{j}^*(\mathrm{I}) = -\mathrm{R\,T\ ln[K(T,p)]}$$

$\mathrm{K}_j(\mathrm{T},p)$ is a measure of the difference in reference chemical potentials of substance j in phases I and II. If the two phases are in equilibrium, there is no affinity for substance j to pass spontaneously between the two phases. At equilibrium, A_j is zero. Hence from equations (c) and (f), for the non-equilibrium state,

$$A_j = RT\,\ln\left[K_j(T,p)\right] + RT\,\ln\left[\frac{x_j(I)\,f_j(I)}{x_j(II)\,f_j(II)}\right]$$

$$\frac{A_j}{T} = R\,\ln\left[K_j(T,p)\right] + R\,\ln\left[\frac{x_j(I)\,f_j(I)}{x_j(II)\,f_j(II)}\right]$$

Equation (g) yields the affinity for chemical substance j to pass between the phases in a non-equilibrium state. In applications of equation (h), we describe the dependence of $(\mathrm{A}_j/\mathrm{T})$ on temperature, pressure and composition of the two phases. In other words we require the general differential of equation (h) which is written in the following form.

$$\begin{aligned} d\left(\frac{A_j}{T}\right) = R\left(\frac{\partial \ln K_j(T,p)}{\partial T}\right) dT \\ + R\left(\frac{\partial \ln K_j(T,p)}{\partial p}\right) dp + R\,d\ln\left[\frac{x_j(I)\,f_j(I)}{x_j(II)\,f_j(II)}\right] \end{aligned}$$

For the transfer process described by $\mathrm{K}_j(\mathrm{T},p)$ we obtain equation (j) where $\Delta_{\mathrm{trans}}\,\mathrm{H_j^0(\ T,p)}$ and $\Delta_{\mathrm{trans}}\,V_j^0(T,p)$ are the standard enthalpy and volume for transfer for chemical substance j.

$$\begin{aligned} \mathrm{d}\left(\frac{\mathrm{A_j}}{\mathrm{T}}\right) = \left(\frac{\Delta_{\mathrm{trans}}\,\mathrm{H_j^0(\ T,p)}}{\mathrm{T^2}}\right) \mathrm{dT} \\ - \left(\frac{\Delta_{\mathrm{trans}}\,\mathrm{V_j^0(\ T,p)}}{\mathrm{T}}\right) \mathrm{dp} + \mathrm{R\,d\ln}\left[\frac{\mathrm{x_j(I)\,f_j(I)}}{\mathrm{x_j(II)\,f_j(II)}}\right] \end{aligned}$$

$\Delta_{\mathrm{trans}}\,\mathrm{H_j^0(\ T,p)}$ and $\Delta_{\mathrm{trans}}\,\mathrm{V_j^0(\ T,p)}$ are properties of pure chemical substance j; i.e. are not dependent on the composition of phases I and II.

Footnotes

[1] Consider the freezing of water;

$$\text{water } (\lambda) \to \text{ water (s)}$$

For this process, $v\left(\mathrm{H_2O};\lambda\right)=-1; v\left(\mathrm{H_2O};\mathrm{s}\right)=1$

The general rule is — Positive for Products. The affinity for spontaneous change,

$$A=-\left(\frac{\partial G}{\partial \xi}\right)_{T,p}=-\sum_{j=1}^{j=i} v_j\,\mu_j=\mu^*\left(H_2\mathrm{O};\lambda\right)-\mu^*\left(H_2\mathrm{O};\mathrm{s}\right)$$

At equilibrium (at fixed T and p), $\mathrm{A}=0$.

$$\text{Then, } \mu^*\left(\mathrm{H_2O};\lambda\right)=\mu^*\left(\mathrm{H_2O};\mathrm{s}\right)$$

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1.2.4: Affinity for Spontaneous Reaction- General Differential

A given closed system is prepared using $\mathrm{n}_{\mathrm{i}}^{0}$ moles of each chemical substance i. At extent of chemical reaction ξ the ratio (A/T) where A is the affinity for spontaneous chemical reaction is defined by independent variables, T, p and ξ.

$$(\mathrm{A}/\mathrm{T}) = (\mathrm{A}/\mathrm{T})[\mathrm{T}, \mathrm{p}, \xi]$$

The general differential of this equation has the following form.[1]

$$\mathrm{d}(\mathrm{A}/\mathrm{T}) = \left[\frac{\partial(\mathrm{A}/\mathrm{T})}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi} \mathrm{dT} + \frac{1}{\mathrm{T}}\left[\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right]_{\mathrm{T},\xi} \mathrm{dp} + \frac{1}{\mathrm{T}}\left[\frac{\partial \mathrm{A}}{\partial \xi}\right]_{\mathrm{T},\mathrm{p}} \mathrm{d}\xi$$

Footnote

[1] Equation (b) forms the basis of equations describing the dependence of A on T at fixed p and on p at fixed T.

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1.2.5: Affinity for Spontaneous Reaction- Dependence on Temperature

Using the definition of the Gibbs energy $\mathrm{G}[=\mathrm{U}+\mathrm{p\,V}-\mathrm{T\,S}=\mathrm{H}-\mathrm{T\,S}]$, we form an equation for the entropy of a closed system. Thus $\mathrm{T\,S}=-\mathrm{G}+\mathrm{H}$. The entropy of the closed system is perturbed by a change in composition/organisation, ξ at fixed T and p.

$$\text{Then, } T\left(\frac{\partial S}{\partial \xi}\right)_{T,p}=-\left(\frac{\partial G}{\partial \xi}\right)_{T,p}+\left(\frac{\partial H}{\partial \xi}\right)_{\mathrm{T,p}}$$

$$\text{But the affinity for spontaneous reaction, } A=-\left(\frac{\partial G}{\partial \xi}\right)_{T,p}$$

A Maxwell equation requires that, $\left(\frac{\partial \mathrm{S}}{\partial \xi}\right)_{\mathrm{T,p}}=\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi}$.

$$\text{Hence, } \mathrm{T}\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi}=\mathrm{A}+\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}}$$

Equation (c) is rearranged to yield the following interesting equation.

\[\mathrm{A}-\mathrm{T} \,\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{p}, \xi}=-\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T}, \mathrm{p}}]

The affinity for spontaneous change and its dependence on temperature are simply related to the enthalpy of reaction at fixed T and p. We exploit this link by considering the derivative $\mathrm{d(A/T)/dT}$ (at fixed p and fixed ξ).

$$\mathrm{d(A/T)/dT}=(1/\mathrm{T})\,(\mathrm{dA/dT})-\mathrm{A/T}^2$$

$$\text{Hence } \left[\frac{\partial(\mathrm{A/T})}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}=-\frac{1}{\mathrm{T}^2}\left[\mathrm{A}-\mathrm{T}\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi}\right]$$

$$\text{Using equation (d), } \left[\frac{\partial(\mathrm{A/T})}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}=\frac{1}{\mathrm{T}^2}\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}}$$

The latter equation is an analogue of the Gibbs-Helmholtz Equation relating the change in Gibbs energy to the enthalpy of reaction, $\left(\frac{\partial H}{\partial \xi}\right)_{T,\mathrm{p}}$. The background to equation (g) is the definition of the dependent variable $(\mathrm{A/T})$ in terms of independent variables, T, p and ξ.

$$\text{Thus} \quad (\mathrm{A/T})=(\mathrm{A/T})[\mathrm{T},\mathrm{p},\xi]$$

The general differential of the latter equation has the following form.

$$\mathrm{d(A/T)}=\left[\frac{\partial(\mathrm{A/T})}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}\mathrm{dT}+\frac{1}{\mathrm{T}}\left[\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right]_{\mathrm{T},\xi}\mathrm{dp}+\frac{1}{\mathrm{T}}\left[\frac{\partial \mathrm{A}}{\partial \xi}\right]_{\mathrm{T,p}}\mathrm{d}\xi$$

But, from equation (e)

$$\mathrm{d(A/T)}=-\left(\mathrm{A/T}^2\right)\,\mathrm{dT}+(1/\mathrm{T})\,\mathrm{dA}$$

$$\text{Or, } \mathrm{dA}=\mathrm{T\,d(A/T)}+(\mathrm{A/T})\,\mathrm{dT}$$

We incorporate equation (i) for the term $(\mathrm{A/T})$. Thus

$$\mathrm{dA}=\left[\frac{1}{\mathrm{T}}\left(\frac{\partial(\mathrm{A/T})}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi}+\frac{\mathrm{A}}{\mathrm{T}}\right]\mathrm{dT}+\left[\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right]_{\mathrm{T},\xi}\mathrm{dp}+\left[\frac{\partial \mathrm{A}}{\partial \xi}\right]_{\mathrm{T,p}}\mathrm{d}\xi$$

Then using equation (g),

$$\mathrm{dA}=\left[\frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}}+\frac{\mathrm{A}}{\mathrm{T}}\right]\mathrm{dT}-\left[\frac{\partial \mathrm{V}}{\partial \xi}\right]_{\mathrm{T,p}}\mathrm{dp}+\left[\frac{\partial \mathrm{A}}{\partial \xi}\right]_{\mathrm{T,p}}\mathrm{d}\xi$$

The latter is a general equation for the change in affinity. We rearrange this equation as an equation for a change in extent of reaction.

$$d\xi = -\left(\frac{\partial \xi}{\partial A}\right)_{T,p}\left[\frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,p} + \frac{A}{T}\right] dT + \left[\frac{\partial V}{\partial \xi}\right]_{T,p}\left(\frac{\partial \xi}{\partial A}\right)_{T,p} dp + \left(\frac{\partial \xi}{\partial A}\right)_{T,p} dA$$

The latter equation has the form of a general differential for the extent of reaction written as,

$$\xi = \xi[T, p, A]$$

$$\text{Or, } d\xi = \left(\frac{\partial \xi}{\partial T}\right)_{p,A} dT + \left(\frac{\partial \xi}{\partial p}\right)_{T,A} dp + \left(\frac{\partial \xi}{\partial A}\right)_{T,p} dA$$

Hence from equation (n),

$$\left(\frac{\partial \xi}{\partial T}\right)_{p,A} = -\left(\frac{\partial \xi}{\partial A}\right)_{T,p}\left[\frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,p} + \frac{A}{T}\right]$$

Equation (q) describes the dependence of extent of reaction on temperature at fixed pressure and affinity for spontaneous reaction. Then from equation (n),

$$\left(\frac{\partial \xi}{\partial p}\right)_{T,A} = +\left[\frac{\partial V}{\partial \xi}\right]_{T,p}\left(\frac{\partial \xi}{\partial A}\right)_{T,p}$$

Equation (r) describes the dependence of extent of reaction at fixed temperature and fixed affinity for spontaneous change.

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1.2.6: Affinity for Spontaneous Reaction - Dependence on Pressure

The Gibbs energy of a given closed system is defined by equation (a) where ξ describes the chemical composition.

$$\mathrm{G} = \mathrm{G}[\mathrm{T}, \mathrm{p}, \xi]$$

We consider the dependence of Gibbs energy on pressure and extent of reaction at fixed temperature T.

$$\frac{\partial}{\partial p}\left(\frac{\partial \mathrm{G}}{\partial \xi}\right) = \frac{\partial}{\partial \xi}\left(\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right)$$

But volume $\mathrm{V} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi}$ and affinity $A = -\left(\frac{\partial G}{\partial \xi}\right)_{\mathrm{T},\mathrm{p}}$.

Volume V and affinity A are given by first differentials of the Gibbs energy, G.

$$\text{Then } -\left(\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} = \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T},\mathrm{p}}$$

Here $\left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T},\mathrm{p}}$ is the volume of reaction, being the increase volume accompanying unit increase in extent of reaction, ξ.

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1.2.7: Affinity for Spontaneous Reaction - Stability

A given closed system at temperature T and pressure p undergoes a spontaneous change in chemical composition. Chemical reaction is driven by the affinity for spontaneous change such that the Gibbs energy decreases.

Thus

$$\mathrm{A} = -\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{\mathrm{T,p}} \tag{1.2.7.1}$$

The plot of Gibbs energy G against composition ξ shows a gradual decrease until G reaches a minimum where the affinity A is zero at chemical equilibrium. An imagined plot beyond equilibrium would show an increase in Gibbs energy. In other words spontaneous chemical reaction stops at the point where G is a minimum (at fixed T and p). If the chemical reaction stops, the rate of chemical reaction is zero. We link the thermodynamic definition of chemical equilibrium and the definition of chemical equilibrium which emerges from the Law of Mass Action with reference to the kinetics of chemical reaction.

An accompanying plot shows a gradually decreasing affinity when plotted against ξ, passing zero at ξ_{eq}. The gradient of the plot in the neighbourhood of equilibrium is negative;

$$\text{i.e. } \left(\frac{\partial \mathrm{A}}{\partial \xi}\right)_{\mathrm{T,p}} < 0 \tag{1.2.7.2}$$

Equation 1.2.7.2 is the thermodynamic condition for a stable chemical equilibrium. The composition does not change no matter how long we wait. Indeed that is the experience of chemists and Equation 1.2.7.2 expresses quantitatively this observation.

One might ask--- how does the system 'know' it is at a minimum in Gibbs energy?

Within the system, any fluctuation in composition leads to an increase in Gibbs energy. This tendency is opposed **spontaneously**; i.e. these fluctuations are opposed.

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1.2.8: Affinity for Spontaneous Chemical Reaction - Law of Mass Action

The differential change in Gibbs energy of a closed system dG is related to the change in chemical composition – organisation using equation (a) where A is the affinity for spontaneous chemical reaction such that $\mathrm{A}\,\mathrm{d}\xi \geq 0$.

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} - \mathrm{A}\,\mathrm{d}\xi \tag{1.2.8.1}$$

Spontaneous chemical reaction is driven by the affinity for spontaneous change, A. Eventually the system reaches a minimum in Gibbs energy G where the affinity for spontaneous change is zero.

$$\text{In general terms, } \mathrm{A}^{\mathrm{eq}} = -\sum \mathrm{v_j}\,\mu_{\mathrm{j}}^{\mathrm{eq}} = 0 \tag{1.2.8.2}$$

We identify chemical equilibrium as the state where the chemical potentials driving the chemical flow from reactants to products are balanced by the chemical potentials driving chemical flow from products to reactants [1]. The condition given in Equation 1.2.8.2 is based on the first and second laws of thermodynamics [1]. These two laws do not lead to quantitative statements concerning the rate of change of chemical composition; i.e. the dependence of the concentration of reactants and products on time.

At a given time t, the rate of change of composition v is defined by equation (c).

$$\mathrm{v} = \mathrm{d}\xi/\mathrm{dt}$$

$$\text{Hence, with } A\,d\xi > 0, A\,V > 0$$

Therefore for chemical reaction in a closed system, the signs of A and v are identical. [1] Moreover if the system is at thermodynamic equilibrium such that A is zero, then v is zero. The latter sentence establishes a crucial link between chemical kinetics and chemical thermodynamics. However away from equilibrium we have no information concerning the rate of change of composition. The required property is the ratio $\mathrm{d}\xi/\mathrm{dt}$ at time t characterising the rate of change of the extent of chemical reaction. Intuitively one might argue that the rate depends on the affinity for spontaneous reaction—the greater the affinity for reaction the faster the reaction. The key equation might take the following form.

$$\mathrm{d}\xi/\mathrm{dt} = \mathrm{L}\,\mathrm{A}$$

Here L is a phenomenological parameter, describing the phenomenon of chemical reaction. Unfortunately no further progress can be made because we have no way of measuring the affinity A for chemical reaction; no affinity meter is available which we can plunge into the reacting system and 'read off' the affinity.[2] In these terms the analysis comes to a halt.

In the context of chemical kinetics, the rate of chemical reaction is defined by equation (f) where n_j refers to the amount of chemical substance j as either product or reactant; positive for product

$$\mathrm{v} = \pm\mathrm{V}^{-1}\,\mathrm{dnn_j}/\mathrm{dt}$$

For chemical reaction involving solutes in dilute solution the volume V of the system (at fixed T and p) is effectively independent of time.

$$\text{Then, } v = \pm\mathrm{dc_j}/\mathrm{dt}$$

The kinetics of chemical reactions in solution are simpler than those for reactions in the gas phase [3] and we confine comment to the former.

The relationship between velocity v and the chemical composition of a solution is described by the Law of Mass Action as proposed by Guldberg and Waage in 1867 [4]. The developments reported by Harcourt and Essen (1867), Bredig and Stern and by Lapworth in 1904 and by Goldschmidt in 1930 were important. Hammett [3] comments that by the 1930s the subject had emerged from the 'dark ages'. Hammett draws attention to the contributions made by Bartlett, Ingold and Pedersen in the decades of 1920 and 1930. Effectively these authors showed that the rate of chemical reaction at time t is a function of the concentrations of substances in the systems at that time, t. In the textbook case the spontaneous chemical reaction [5,6] between two chemical substances X and Y at fixed T and p in aqueous solution, has the following form.

$$\mathrm{x.X(aq) + y.Y(aq) -\!> \ products}$$

$$\text{Rate of reaction } = \mathrm{k}\,[\mathrm{X}]^{\alpha}\,[\mathrm{Y}]^{\beta}$$

Here α and β are orders of reaction with respect to substances X and Y. These orders have to be determined from the experimental kinetic data because they do not necessarily correspond to the stoichiometric coefficients in the chemical equation [7].

We develop the argument by considering a chemical reaction in solution. An aqueous solution is prepared containing n1 moles of water(l) and $\mathrm{n_X^0}$ moles of chemical substance X at time, $t = 0$ where $n_X^0 >> n_1$. Spontaneous chemical reaction leads to the formation of product Y, where at '$t = 0$', $\mathrm{n_Y^0}$ is zero. Chemical reaction is described using equation (j).

$$\begin{array}{lccc} & \mathrm{X(aq)} & \rightarrow & \mathrm{Y(aq)} \\ \mathrm{Att} = 0 & \mathrm{n_X^0} & \mathrm{n_y^0} = 0 & \mathrm{mol} \end{array}$$

The convention is for the chemical reaction to be written in the form 'reactants → products', such that the affinity for reaction A is positive and hence $\mathrm{d}\xi$ and $\mathrm{d}\xi/\mathrm{dt}$ are positive. Many chemical reactions of the form shown in equation (j) go to completion.

$$\mathrm{Thus\ \ lim\,it(t \rightarrow \infty) n_X = 0; n_Y = n_X^0}$$

The minimum in Gibbs energy (where $\mathrm{A} = 0$) is attained when all reactant has been consumed.

First Order Reactions

A given closed system contains $\mathrm{n_X^0}$ moles of chemical substance X which X decomposes to form chemical substance Z. At time t, ξ moles of reactant X have formed product Z.

\multicolumn1c Chemical Reaction	X	Z
Amounts at t = 0;	$\mathrm{n_X^0}$	0 mol
Concentrations (t = 0)	$\mathrm{n_X^0/V}$	0 mol $\mathrm{m^{-3}}$
At time t	$\mathrm{n_X^0} - \xi$	mol
Amounts	$\left(\mathrm{n_X^0} - \xi\right)/\mathrm{V}$	ξ/Vmolm

The law of mass action is the extra-thermodynamic assumption which relates the rate of change of concentration t o the composition of the system.

$$\mathrm{Then,\ } -\frac{\mathrm{d}\left[\left(\mathrm{n_X^0} - \xi\right)/\mathrm{V}\right]}{\mathrm{dt}} = \frac{\mathrm{d}[\xi/\mathrm{V}]}{\mathrm{dt}} = \mathrm{k}\,\frac{\left[\mathrm{n_X^0} - \xi\right]}{\mathrm{V}}$$

The constant of proportionality, rate constant k, in this case has units of $\mathrm{s^{-1}}$.

$$\mathrm{Then\ in\ terms\ of\ reactant\ X,\ } \frac{\mathrm{d}\xi}{\mathrm{dt}} = \mathrm{k}\ \left[\mathrm{n_X^0} - \xi\right]$$

Chemical reaction proceeds leading to a decrease in the Gibbs energy of the system until $\mathrm{n_X^0} = \xi$ such that all reactant has been consumed. At this point $(\mathrm{d}\xi/\mathrm{dt})$ is zero, the system is at chemical equilibrium and the Gibbs energy is a minimum. Further from equation (m),

$$\int_{\xi=0}^{\xi} \frac{d\xi}{\left(n_X^0 - \xi\right)} = \int_{t=0}^{t} k\,dt$$

The Law of Mass Action is the most important extra-thermodynamic equation in chemistry.

Second Order Reactions

A given closed system contains $\mathrm{n_X^0}$ and $\mathrm{n_Y^0}$ moles of chemical substances X and Y respectively at fixed T and p. Spontaneous chemical reaction produces chemical substance Z. At time t, ξ moles of product Z are formed from chemical substances X and Y.

c Chemical Reaction	X	+Y	Z
Amounts at t = 0;	$\mathrm{n_X^0}$	$\mathrm{n_Y^0}$	0 mol
Concentrations (t = 0)	$\mathrm{n_X^0/V}$	$\mathrm{n_Y^0/V}$	0 mol m
At time t			
Amounts	$\mathrm{n_X^0} - \xi$	$\mathrm{n_Y^0} - \xi$	ξmol
Concentrations	$\left(\mathrm{n_X^0} - \xi\right)/\mathrm{V}$	$\left(\mathrm{n_Y^0} - \xi\right)/\mathrm{V}$	ξ/Vmolm

The Law of Mass Action is the extra-thermodynamic assumption, relating the rate of change of concentration to the composition of the system. Then,

$$-\frac{\mathrm{d}\left[\left(\mathrm{n_X^0}-\xi\right)/\mathrm{V}\right]}{\mathrm{dt}}=-\frac{\mathrm{d}\left[\left(\mathrm{n_Y^0}-\xi\right)/\mathrm{V}\right]}{\mathrm{dt}}=\frac{\mathrm{d}[\xi/\mathrm{V}]}{\mathrm{dt}}=\mathrm{k}\,\frac{\left[\mathrm{n_X^0}-\xi\right]}{\mathrm{V}}\,\frac{\left[\mathrm{n_Y^0}-\xi\right]}{\mathrm{V}}$$

The unit of rate constant k is '$\mathrm{m^3\ mol^{-1}\ s^{-1}}$'.

$$\text{Then, } \frac{\mathrm{d}\xi}{\mathrm{dt}}=\mathrm{k\,V^{-1}}\ \left[\mathrm{n_X^0}-\xi\right]\ \left[\mathrm{n_Y^0}-\xi\right]$$

$$\text{Or, }\quad \int_{\xi=0}^{\xi}\frac{\mathrm{d}\xi}{\left[n_X^0-\xi\right]\ \left[n_Y^0-\xi\right]}=\int_{t=0}^{t}k\,V^{-1}\,dt$$

In applications of equation (q), rate constant k and volume V are usually treated as independent of time.[8]

The foregoing analysis of kinetics of chemical reactions illustrates the application of the variable ξ in describing the composition of a closed system. Most accounts of chemical kinetics start out with a consideration of concentrations of chemical substances in a given system. [9,10]

Nevertheless for each and every chemical reaction, the form of the relevant 'Law of Mass Action' has to be determined from the observed dependence of composition on time. The latter sentence does not do justice to the skills of chemists in this context.

Reaction to Chemical Equilibrium

In the previous section we considered those cases where chemical reaction goes to completion in that one or more of the reactants are consumed. For many cases this is not the case. Here we imagine that a dilute solution has been prepared using $\mathrm{n_X^0}$ and $\mathrm{n_Y^0}$ moles of solute reactants X and Y. Chemical reaction at fixed T and p proceeds spontaneously. The Gibbs energy of the system decreases reaching a minimum where the affinity for spontaneous reaction is zero. Chemical analysis shows that the resulting system contains product Z together with reactants X and Y, and that the chemical composition is independent of time; i.e. chemical kinetic equilibrium. Thus,

$$\begin{array}{ccccccc}
 & \mathrm{X(aq)} & + & \mathrm{Y(aq)} & \Leftrightarrow & \mathrm{Z(aq)} & \\
\mathrm{Att}=0 & \mathrm{n_X^0} & \mathrm{n_Y^0} & \mathrm{n_Y^e}=\mathrm{n_Y^0}-\xi^{\mathrm{eq}} & & \mathrm{n_{eq}^{eq}}=\xi^{\mathrm{eq}} & \mathrm{mol} \\
 & \mathrm{Att}=\infty & & \mathrm{n_x^{eq}}=\mathrm{n_X^0}-\xi^{\mathrm{eq}} & & \mathrm{n_{eq}} & \\
\text{or,} & \mathrm{c_X^{eq}}=\left(\frac{\mathrm{n_X^0}-\xi^{\mathrm{eq}}}{\mathrm{V}}\right) & & \mathrm{c_{eq}^{eq}}=\left(\frac{\mathrm{n_Y^0}-\xi^{\mathrm{eq}}}{\mathrm{V}}\right) & & \mathrm{c_Z^{eq}}=\left(\frac{\xi^{\mathrm{eq}}}{\mathrm{V}}\right) &
\end{array}$$

A number of assumptions are based on the Law of Mass Action. $\mathrm{At\ time}\ t,\ \mathrm{rate\ of\ forward\ reaction}\ = k_f\ \ c_X(t)\ c_Y(t)$ and rate of the reverse reaction $= \mathrm{k_r\,c_Z(t)}$

Rate constants $\mathrm{k_f}$ and $\mathrm{k_r}$ are initially assumed to be independent of the extent of reaction. A key conclusion is now drawn. Because at '$t \rightarrow$ infinity', the properties of the system are independent of time, the system is 'at chemical equilibrium where the rates of forward and reverse reactions are balanced.

$$\text{Then, } \mathrm{k_f^{eq}\,c_X^{eq}\,c_Y^{eq}=k_r^{eq}\,c_z^{eq}}$$

$$\text{Hence,}\quad \mathrm{d\xi^{eq}/dt}=0$$

$$\text{and } \mathrm{k_{eq}^{eq}}\left(\frac{\mathrm{n_X^0}-\xi^{\mathrm{eq}}}{\mathrm{V}}\right)\left(\frac{\mathrm{n_Y^0}-\xi^{\mathrm{eq}}}{\mathrm{V}}\right)=\mathrm{k_r^{eq}}\,\frac{\xi^{\mathrm{eq}}}{\mathrm{V}}$$

At this point we encounter a key problem -- we cannot determine \(\mathrm{k}_{\mathrm{f}}^{\mathrm{eq}}\) and \(\mathrm{k}_{\mathrm{r}}^{\mathrm{eq}}\) because at equilibrium the composition of the system is independent of time. Nevertheless we can express the ratio of rate constants as a function of the composition at equilibrium.

$$\left(\mathrm{k_f^{eq}/k_r^{eq}}\right)\left(\frac{\mathrm{n_X^0}-\xi^{\mathrm{eq}}}{\mathrm{V}}\right)\left(\frac{\mathrm{n_Y^0}-\xi^{\mathrm{eq}}}{\mathrm{V}}\right)=\frac{\xi^{\mathrm{eq}}}{\mathrm{V}}$$

The ratio k_f^{eq}/k_r^{eq} is characteristic of the system (at defined T and p), defining what we might call a 'Law of Mass Action equilibrium constant', $K(lma)$.

$$\text{Thus } K(\text{lm}\, a) = k_f^{eq}/k_r^{eq}$$

In other words, the property $K(lma)$ is based on a balance of reaction rates whereas the thermodynamic equilibrium constant is based on a balance of chemical potentials. With reference to equation (v), at fixed T and p, the thermodynamic condition is given in equation (w).

$$\mu_X^{eq}(aq) + \mu_Y^{eq}(aq) = \mu_Z^{eq}(aq)$$

$$\text{For } p \cong p^0,\ K^0(T) = \frac{(m_Z\, \gamma_Z/m^0)^{eq}}{(m_X\, \gamma_X/m^0)^{eq}\ (m_Y\, \gamma_Y/m^0)^{eq}}$$

Therefore the question is raised--- how is $K(lma)$ related to $K^0(T)$? In the absence of further information, a leap of faith by chemists sets $K(lma)$ equal to $K^0(T)$. We avoid debating the meaning of the phrase 'rate constants at equilibrium' [7].

Energy of Activation

Spontaneous chemical reaction involving a single solute $X(aq)$ can be described using a rate constant k for a solution at fixed T and p where the concentration of solute X at time t is $c_X(aq)$.

If we can assume that in solution there are no solute-solute interactions, rate constant k is not dependent on the composition of the solution. In thermodynamic terms, the thermodynamic properties of solute X are ideal; for such a system rate constant k is independent of time and initial concentration of solute X. In other words experiment yields the property $k(T, p)$ for a given solution indicating that the rate constant is a function of temperature and pressure. For nearly all chemical reactions in solution rate constants increase with increase in temperature, a dependence described by the Arrhenius equation. [11]

$$k = A\, \exp(-E_A/R\, T)$$

Then rate constant, k increases with increase in temperature. The idea emerges that spontaneous conversion of reactant to products is inhibited by an 'energy' barrier. Further in the $\text{limit}(T \to \infty)\, \ln(k) = A$, the pre-exponential factor which has the same units as rate constant k.

The assumption in the foregoing comments is that E_A is independent of temperature such that for example a first order rate constant $\ln(k/s^{-1})$ is a linear function of T^{-1}.

$$\text{Thus,} \quad \ln(k/s^{-1}) = \ln(A/s^{-1}) - (E_A/R\, T)$$

The latter pattern is generally observed but there are many well-documented cases where the plot is not linear. In other words it is incorrect to conclude that equation (y) somehow predicts how rate constants depend on temperature. There is no substitute for actually measuring this dependence.

Transition State Theory

The law of mass action and the concept of an activation energy for a given chemical reaction are extrathermodynamic. This conclusion is unfortunate, implying that the treatment of kinetic data for reactions in solution is completely divorced from the thermodynamic treatment of the properties of solution. One can understand therefore why Transition Sate Theory (TST) attracts so much interest.[12,13] At the very least, this theory offers analysis of kinetic data a patina of thermodynamic respectability. We describe TST with respect to a chemical reaction where the dependence of composition on time is described using a first order rate constant.

For chemical reactions in the gas phase, statistical thermodynamics offers a reasonably straightforward approach to the description of both reactants and a transition state in which one vibrational mode for the transition state is transposed into translation along the reaction co-ordinate. The theory was re-expressed in terms of equations which could be directly related to the thermodynamics of the process of reaction in solutions.

Chemical reaction proceeds from reactant $X(aq)$ to products through a transition state $X^{\neq}(aq)$. As the reaction proceeds the amount of solute X, $n_X(aq)$ decreases but at all times reactant $X(aq)$ and transition state $X^{\neq}(aq)$ are in chemical equilibrium.

$$\text{Thus } \mathrm{X(aq)} \Leftrightarrow = \mathrm{X}^{7} \rightarrow \text{ products}$$

The condition 'chemical equilibrium' is quantitatively expressed in terms of chemical potentials.

$$\mu_{\mathrm{X}}^{\mathrm{eq}}(\mathrm{aq;T;p}) = \mu_{\neq}^{\mathrm{eq}}(\mathrm{aq;T;p})$$

Conventionally where kinetics of reactions in solution are addressed, the composition of solutions is expressed in terms of concentrations using the unit, moldm^{-3}. Then equation (zc) is formed assuming that ambient pressure is close to the standard pressure, p^0; $\mathrm{c_r} = 1\ \mathrm{moldm}^{-3}$. Hence,

$$\mu_{\mathrm{X}}^{0}(\mathrm{aq;T}) + \mathrm{R\,T\ ln}\left(\mathrm{c_X\,y_X/c_r}\right)^{\mathrm{eq}} = \mu_{\neq}^{0}(\mathrm{aq;T}) + \mathrm{R\,T\ ln}\left(\mathrm{c_{\neq}\,y_{\neq}/c_r}\right)^{\mathrm{eq}}$$

The standard Gibbs energy of activation $\Delta^{\neq}\mathrm{G}^{0}(\mathrm{aq;T})$ is given by equation (zd) leading to the definition of an equilibrium constant ${}^{*}\,\mathrm{K}^{0}(\mathrm{aq;T});\ \text{with } \mathrm{p} \approx \mathrm{p}^{0}$.

$$\Delta^{\neq}\mathrm{G}^{0}(\mathrm{aq;T}) = \mu_{\neq}^{0}(\mathrm{aq;T}) - \mu_{\mathrm{X}}^{0}(\mathrm{aq;T})$$

$$\text{Then} \quad \Delta^{\neq}\mathrm{G}^{0}(\mathrm{aq;T}) = -\mathrm{R\,T\ ln}\left(\mathrm{c_{\neq}\,y_{\neq}/c_X\,y_X}\right)^{\mathrm{eq}}$$

$$\text{By definition, } \Delta^{\neq}\mathrm{G}^{0}(\mathrm{aq;T}) = -\mathrm{R\,T\ ln}\left[{}^{\neq}\mathrm{K}^{0}(\mathrm{aq;T})\right]$$

$$\text{Therefore, } \mathrm{c_{\neq}} = {}^{\neq}\mathrm{K}^{0}(\mathrm{aq;T})\,\mathrm{c_X\,y_X/y_{\neq}}$$

Through the course of chemical reaction, as the concentration of reactant $\mathrm{X(aq)}$ decreases, the condition given in equation (zb) holds. Chemical reaction is not instantaneous because $\mu_z^0(\mathrm{aq;T}) > \mu_{\mathrm{X}}^0(\mathrm{aq;T})$; a barrier exists to chemical reaction. Consequently the concentration $\mathrm{c_{\neq}}$ is small. The analysis up to equation (zf) is based on a thermodynamic description of equilibrium between reactant and transition states. In the limit that the solution is very dilute, $y_X = y_{\neq} = 1$ at all time t, T and p.

$$\text{Thus at given } T \text{ and } p, [14] \quad k = \frac{k_B T}{h} \exp\left(\frac{-\Delta^{\neq}G^{0}}{RT}\right)$$

$$\text{Then, } \mathrm{k} = \frac{\mathrm{k_B\,T}}{\mathrm{h}} \exp\left(-\frac{\Delta^{\neq}\mathrm{H}^{0}}{\mathrm{R\,T}} + \frac{\Delta^{\neq}\mathrm{S}^{0}}{\mathrm{R}}\right)$$

$\Delta^{\neq}\mathrm{G}^{0}$ is the standard Gibbs energy of activation defined in terms of reference chemical potentials of transition state and reactants. Here $\mathrm{k_B}$ is the Boltzmann constant and h is Planck's constant [15].

$$\Delta^{\neq}\mathrm{G}^{0} = -\mathrm{R\,T\ ln}\left(\frac{\mathrm{h\,k(T)}}{\mathrm{k_B\,T}}\right)$$

At temperature T, $\Delta^{\neq}\mathrm{G}^{0}(\mathrm{aq;T})$ is re-expressed in terms of standard enthalpy and standard entropy of activation [16].

$$\text{Then, } \Delta^{\neq}\mathrm{G}^{0}(\mathrm{aq;T}) = \Delta^{\neq}\mathrm{H}^{0}(\mathrm{aq;T}) - \mathrm{T}\,\Delta^{\neq}\mathrm{S}^{0}(\mathrm{aq;T})$$

The standard isobaric heat capacity of activation [17,18],

$$\Delta^{\neq}\mathrm{C_p^0(aq)} = \left(\frac{\partial\Delta^{\neq}\mathrm{H}^{0}(\mathrm{aq})}{\partial\mathrm{T}}\right)_{\mathrm{p}}$$

In summary transition state theory allows kinetic data to be analysed using the protocols and equations of thermodynamics.

Analysis of the dependence of rate constants at fixed temperature as a function of pressure yields standard volumes of activation $\Delta^{\neq}\mathrm{V}^{0}(\mathrm{aq;T})$. In further exercises this volumetric parameter is measured as functions of pressure at temperature T and of temperature at fixed pressure [20].

Nevertheless a word of caution is in order. Johnston [21] points out that diagrams describing the progress of chemical reaction through several intermediates are often misleading. Such diagrams should be based on reference chemical potentials otherwise misleading conclusions can be drawn; see also [22 - 28].

Footnotes

[1] I. Prigogine and R. Defay, Chemical Thermodynamics, trans. D. H. Everett, Longmans Green, London , 1953.

[2] In fact in the treatment of data obtained using fast reaction techniques (e.g. temperature jump and pressure-jump) where the displacement from equilibrium is small, it is assumed that the rate of response is linearly related to the affinity for chemical reaction. (a) E. F. Caldin, Fast Reactions in Solution, Blackwell, Oxford, 1964. (b) M. J. Blandamer, Introduction to Chemical Ultrasonics, Academic Press, London, 1973.

[3] L. P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, 1970, 2nd. Edition.

[4] K. J. Laidler, [The World of Physical Chemistry, Oxford University Press, Oxford, 1993,page 115] comments
'Neither did they (i.e. Guldberg and Waage] make any contributions to kinetics since they worked in terms of forces and not of rates, although they did tentatively suggest that rates might be proportional to forces'.

[5] The condition 'spontaneous change' signals a 'natural' direction but that does mean that the process is instantaneous. The properties of the system are dependent on time. We make this point to counter such statements as 'Thermodynamics … deals exclusively with system showing no temporal change; reacting systems are outside its province'; cf. E. A. Moelwyn-Hughes, Kinetics of Reactions in Solution, Clarendon Press, Oxford, 1947, page 162.

[6] Thermodynamics in the form of the first and second laws offers no way forward. Intuitively one might argue that the rate of change of composition would be directly related to the affinity for spontaneous reaction, A where π is a proportionality factor characteristic of the system, temperature and pressure.

$$\text{Thus, } \mathrm{d}\xi/\mathrm{dt} = \pi\,\mathrm{A} \quad \text{where} \quad \lim \mathrm{it}(\mathrm{A} \to 0)\mathrm{d}\xi/\mathrm{dt} = 0$$

In fact we might draw an analogy with Ohm's law whereby electric current i (= rate of flow of charge) is proportional to the electric potential gradient, $\Delta\phi$, the constant of proportionality being the electrical conductivity, L; $\mathrm{i} = \mathrm{L}\,\Delta\phi$ where L is characteristic of the system, temperature and pressure. Indeed such a kinetic force-flow link might be envisaged. Indeed an link emerges with the phenomenon of electric potential driving an electric current through an electrical circuit.

Electric current = rate of flow of charge, unit = Ampere.

Electric potential has the unit, volt.

The product, I.\(\mathrm{V} = [\mathrm{A}]\ [\mathrm{JA}^{-1}\ \mathrm{s}^{-1}] = [\mathrm{W}]$
Here W is the SI symbol for the unit of **power**, watt.
Rate of chemical reaction $\mathrm{d}\xi/\mathrm{dt} = [\mathrm{molss}^{-1}]$
Affinity $\mathrm{A} = [\mathrm{Jmol}^{-1}]$
Then $\mathrm{A}\ \mathrm{d}\xi/\mathrm{dt} = [\mathrm{Jmolm}^{-1}]\ [\mathrm{mols}^{-1}] = [\mathrm{W}]$
Interestingly chemists rarely refer to the 'wattage' of a chemical reaction.

[7] One cannot help be concerned with accounts which describe chemical equilibrium in terms of rates of chemical reaction. As we understand the argument runs along the following lines. For a chemical equilibrium having the following stochiometry, $\mathrm{X} + \mathrm{Y} \Leftrightarrow \mathrm{Z}$ at equilibrium the rates of forward and reverse reactions are balanced.

$$\mathrm{k_f}\,[\mathrm{X}]\,[\mathrm{Y}] = \mathrm{k_r}\,[\mathrm{Z}]$$

Here $\mathrm{k_f}$ and $\mathrm{k_f}$ are the forward and reverse rate constants.

$$\text{Then } \mathrm{K} = \mathrm{k_f}/\mathrm{k_r} = [\mathrm{Z}]/[\mathrm{X}]\,[\mathrm{Y}]$$

The argument loses some of its force if one turns to accounts dealing with chemical kinetics when questions of order and molecularity are raised. In any case one cannot measure rates of chemical reactions 'at equilibrium' because at equilibrium 'nothing is happening'. Even in those cases where the rates of chemical reactions 'at equilibrium ' are apparently measured the techniques rely on following the return to equilibrium when the system is perturbed.

[8] In nearly all applications of the law of mass action to chemical reactions in solution a derived rate constant is based on on a description of the composition on time at fixed T and p. Therefore the calculated rate constant is an isobaric-isothermal property of the system. Nevertheless the volume is usually taken as independent of time. Certainly in most applications in solution chemistry

the solutions are quite dilute and so throughout the course of the reaction the volume is effectively constant. An interesting point now emerges in that a given rate constant is an isothermal-isobaric-isochoric property.

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[11] $\mathrm{E_A} = \left[\mathrm{Jmol^{-1}}\right]$ such that $\mathrm{E_A/R\,T} = \left[\mathrm{Jmol^{-1}}\right] / \left[\mathrm{JK^{-1}\ mol^{-1}}\right]\ [\mathrm{K}] = [1]$

[12] The account given here stresses the link with classical thermodynamics. The key equations should be developed using statistical thermodynamics; see H. Eyring, J. Chem. Phys., 1935, **3**,107.

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[15] $\frac{\mathrm{k_B\,T}}{\mathrm{h}}\,\mathrm{c_{\neq}} = \left[\mathrm{s^{-1}}\right]\ \left[\mathrm{moldm^{-3}}\right] = \left[\mathrm{moldm^{-3}\ s^{-1}}\right]$

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1.2.9: Affinity for Spontaneous Chemical Reaction - Isochoric Condition and Controversy

According to the First and Second Laws of thermodynamics, the change in Helmholtz energy dF accompanying chemical reaction, change in volume and change in temperature is given by Equation 1.2.9.1.

$$\mathrm{dF} = -\mathrm{S}\,\mathrm{dT} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi \tag{1.2.9.1}$$

where,

$$\mathrm{A}\,\mathrm{d}\xi \geq 0$$

At constant T and V:

$$\mathrm{dF} = -\mathrm{A}\,\mathrm{d}\xi; \mathrm{A}\,\mathrm{d}\xi \geq 0$$

If we monitor the change in composition of a closed system held at constant temperature and constant volume, equilibrium corresponds to a minimum in Helmholtz energy. In practice chemists concerned with spontaneous chemical reaction in solutions held at constant temperature, do not constrain the system to a constant volume. Rather they constrain the system to constant temperature and pressure. Therefore the following equation is the key.

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} - \mathrm{A}\,\mathrm{d}\xi$$

$$\text{At constant } \mathrm{T} \text{ and } \mathrm{p}, \mathrm{dG} = -\mathrm{A}\,\mathrm{d}\xi; \quad \mathrm{A}\,\mathrm{d}\xi \geq 0$$

The rate at which chemical reaction drives the system to a minimum in Gibbs energy is described by the Law of Mass Action. Presumably a similar law would describe the approach to equilibrium of a system held at constant T and V, the system moving spontaneously towards a lower Helmholtz energy. We do not explore this point. Nevertheless the isochoric condition is often invoked and we examine how this comes about.

(a) Chemical Kinetics

A key problem revolves around the role of the solvent in determining activation parameters; e.g. standard Gibbs energy of activation and standard enthalpy of activation. An extensive literature examines the role of solvents. But densities of solvents are a function of temperature and pressure. Then in attempting to understand the factors controlling kinetic activation parameters there is the problem that intermolecular distances (e.g. solvent-solvent and solvent-solute) are a function of temperature. In 1935 Evans and Polanyi [1] suggested that isochoric activation parameters for chemical reaction in aqueous solution might be more mechanistically informative than conventional isobaric activation parameters; *i.e.* $[\partial \ln(\mathrm{k})/\partial \mathrm{T}]_{\mathrm{V}}$ rather than $[\partial \ln(\mathrm{k})/\partial \mathrm{T}]_{\mathrm{p}}$ where k is the rate constant for spontaneous chemical reaction [2,3].

With reference to chemical reactions in dilute aqueous solution the isochoric standard internal energy of activation $\Delta^{\neq}\mathrm{U}^{0}_{\mathrm{V}}$ is related to the isobaric standard enthalpy of activation $\Delta^{\neq}\mathrm{H}^{0}_{\mathrm{p}}$ at temperature T and the standard volume of activation $\Delta^{\neq}V^{0}$ using equation (f) where α^{*}_{p1} and κ^{*}_{T1} are respectively the isobaric expansibilities and isothermal compressibilities of water.

$$\Delta^{\neq}\mathrm{U}^{0}_{\mathrm{V}} = \Delta^{\neq}\mathrm{H}^{0}_{\mathrm{p}} - \mathrm{T}\,\left[\alpha^{*}_{\mathrm{p1}}/\kappa^{*}_{\mathrm{T1}}\right]\,\Delta^{\neq}\mathrm{V}^{0}$$

Baliga and Whalley [4] noted that the dependence on solvent mixture composition of $\Delta^{z}\mathrm{U}^{0}_{\mathrm{V}}$ is less complicated than that for $\Delta^{\neq}\mathrm{H}^{0}_{\mathrm{p}}$ for solvolysis of benzyl chloride in ethanol + water mixtures at $298.15\ \mathrm{K}$. A similar pattern was reported by Baliga and Whalley [5] for the hydrolysis of 2-chloro-2-methyl propane in the same mixture at $273.15\ \mathrm{K}$. [6]

The proposal concerning isochoric activation parameters sparked enormous interest and debate.[7-13] Much of the debate centred on the isochoric condition and the answer to the question ‘what volume is held constant?’ With reference to equation (f), α^{*}_{pl} and κ^{*}_{T1} depend on temperature. Then the volume identified by subscript V on $\Delta^{\neq}\mathrm{U}^{0}_{\mathrm{V}}$ is dependent on temperature. Further the molar volumes of binary liquid mixtures depend on T and p. In other words the isochoric condition is not global across the given data set. Haak et al. noted [14] that either side of the TMD of water there are pairs of temperatures where the molar volumes of water at ambient pressure are equal. Hence rates of reaction for chemical reactions in dilute aqueous solution at such temperatures would yield pairs of isochoric rate constants. Kinetic data for spontaneous hydrolysis of 1–benzoyl–1,2,4 triazole in aqueous solution at closely spaced temperatures close to the TMD of water reveal no unique features associated with the isochoric condition.[15]

The isochoric condition nevertheless remains interesting. There is however an important point to note. For the most part kinetic experiments investigate the rates of chemical reactions in solution at constant T and p. In other words spontaneous change is driven by the decrease in Gibbs energy. The latter is the operating thermodynamic potential function, both T and p being held constant; the rate constant is an isobaric-isothermal property. Further the dependence of rate constant is often monitored on temperature at constant pressure, recognising that the volume of the system changes as the temperature is altered.

In principle spontaneous chemical reaction could be monitored, holding the system at constant T and volume V. Here the direction of spontaneous chemical reaction would be towards a minimum in Helmholtz energy, F. The dependence of the isochoric – isothermal rate constant on temperature could again in principle be measured. The technological challenge would be immense because one might expect enormous pressures to be required to hold the volume constant when the temperature was increased.

Similar concerns over the definition of isochoric emerge in the context of the dependence on T and p of acid dissociation constants in aqueous solution of ethanoic acid [16].

(a) Electrical Mobilities

The migration of ions through a salt solution under the influence of an applied electric potential can be envisaged as a rate process, analogous to the rate of chemical reaction. In most studies the applied electric field is weak such that the ions are only marginally displaced from their 'equilibrium' positions. The derived property is the molar conductivity [17] characterising a given salt in solution at defined T and p.

$$\text{Then,} \quad \ln(\Lambda) = \ln(\Lambda[\mathrm{T}, \mathrm{p}])$$

The isobaric dependence of $\ln(\Lambda)$ on temperature yields the isobaric energy of activation $\mathrm{E_p}$[18] $\left[= \mathrm{R}\left\{\partial \ln\left(\Lambda^0\right)/\partial(1/\mathrm{T})\right\}_\mathrm{p}\right]$. An extensive literature [19] describes the isochoric energies of activation defined by equation (h).

$$\mathrm{E_V} = -\mathrm{R}\,\mathrm{T}^2\left\{\partial \ln\left(\Lambda^0\right)/\partial\right\}_\mathrm{V}$$

The property $\mathrm{E_V}$ has attracted considerable attention and debate [18-,21]. Nevertheless the same question (i.e. which volume is held constant?) can be asked. The debate emerges partly form the observation that T and p are intensive variables whereas V is an extensive variable.

Footnotes

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SECTION OVERVIEW

1.3: Calorimeter

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1.3.4: Calorimetry- Solutions- Adiabatic

1.3.5: Calorimetry- Solutions - Heat Flow

1.3.6: Calorimetry - Titration Microcalorimetry

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1.3.10: Calorimetry- Solutions- Flow Microcalorimetry

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1.3.1: Calorimeter- Isobaric

An isobaric calorimeter is designed to measure the heat accompanying the progress of a closed system from state (I) to state (II) at constant pressure. [1] It follows from the first law that if only '$p-\mathrm{V}$' work is involved,

$$\Delta \mathrm{U} = \mathrm{q} - \mathrm{p}\,\Delta \mathrm{V}$$

By definition the enthalpy H of a closed system is given by equation (b);

$$\mathrm{H} = \mathrm{U} + \mathrm{p}\,\mathrm{V}$$

$$\text{Then, } \Delta \mathrm{H} = \Delta \mathrm{U} + \mathrm{p}\,\Delta \mathrm{V} + \Delta \mathrm{p}\,\mathrm{V}$$

Hence from equations (a) and (c), at constant pressure,

$$\Delta \mathrm{H} = \mathrm{q}$$

$$\text{Thus at constant pressure, } \Delta \mathrm{H} = \mathrm{H(II)} - \mathrm{H(I)} = \mathrm{q}$$

Hence if we record the heat (exothermic or endothermic) at constant pressure we have the change in enthalpy, $\Delta \mathrm{H}$. [2] Equation (e) highlights the optimum thermodynamic equation. On one side of the equation is a measured property/change and on the other side of the equation is a change in a property of the system which we judge to be informative about the chemical properties of a system; e.g. $\Delta \mathrm{H}$. The problem is that the derived property is not the actual change in energy, $\Delta \mathrm{U}$.

Footnotes

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1.3.2: Calorimetry- Isobaric- General Operation

Calorimetry, particularly isobaric calorimetry, is a key technique in chemical thermodynamics, for studying the properties of liquid mixtures and solutions. Numerous designs for calorimeters have been published. [1,2] The operation of a classic calorimeter involves two key steps.

Step 1. Known amounts of two liquids (e.g. solvent and solution) are mixed in a thermally insulated reaction vessel at constant pressure. The rise in temperature is recorded.

Step 2. A known electric current is passed for a recorded length of time through an electric resistance in the reaction vessel to produce a comparable rise in temperature.

By proportion the required amount of energy to produce the measured rise in temperature in step 1 is obtained. [Complications emerge by the need to take account of spontaneous cooling in both steps when the temperature of the calorimeter exceeds ambient temperature; cf. Newton's Law of Cooling.]

Another type of isobaric calorimeter involves injecting aliquots of one liquid (solution or solvent) into sample cell containing another liquid, recording the rise in temperature accompanying injection of each aliquot. The calorimeter is again calibrated electrically.

Footnotes

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1.3.3: Calorimetry- Solutions- Isobaric

Classic (isobaric) calorimetric experiments often centre on the determination of the change in enthalpy ΔH for a given well-defined process. For example, the heat accompanying the mixing of known amounts of two liquids [e.g. water(λ) and ethanol(λ)] to form a binary liquid mixture yields the enthalpy of mixing, $\Delta_{\text{mix}}\text{H}$. Similarly enthalpies of solution are obtained by recording the heat accompanying the solution of a known amount of solute (e.g. urea) in a known amount of solvent; e.g. water(λ). Key equations emerge from the following analysis.

The enthalpy H of a closed system is an extensive function of state which for a closed system is defined by the set of independent variables, T, p and ξ where ξ represents the chemical composition.

$$\text{H} = \text{H}[\text{T}, \text{p}, \xi] \tag{1.3.3.1}$$

Equation 1.3.3.2 is the complete differential of Equation 1.3.3.1.

$$\text{dH} = \left(\frac{\partial \text{H}}{\partial \text{T}}\right)_{\text{p},\xi} \text{dT} + \left(\frac{\partial \text{H}}{\partial \text{p}}\right)_{\text{T},\xi} \text{dp} + \left(\frac{\partial \text{H}}{\partial \xi}\right)_{\text{T,p}} \text{d}\xi \tag{1.3.3.2}$$

If the closed system is held at constant pressure (e.g. ambient) the differential enthalpy dH equals the heat dq.

$$T\text{dq} = \left(\frac{\partial \text{H}}{\partial \text{T}}\right)_{\text{p},\xi} \text{dT} + \left(\frac{\partial \text{H}}{\partial \xi}\right)_{\text{T,p}} \text{d}\xi$$

Here $\left(\frac{\partial \text{H}}{\partial \text{T}}\right)_{\text{p},\xi}$, is the differential dependence of enthalpy H on temperature at constant pressure and composition whereas $\left(\frac{\partial H}{\partial \xi}\right)_{\text{T,p}}$, is the differential dependence of enthalpy H on composition at fixed temperature and pressure.

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1.3.4: Calorimetry- Solutions- Adiabatic

A general equation describes heat q in terms of changes in temperature and composition at constant pressure; $\mathrm{dH} = q$.

$$\mathrm{dq} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi} \mathrm{dT} + \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} \mathrm{d}\xi \tag{1.3.4.1}$$

In this application of Equation 1.3.4.1, the system is thermally insulated; i.e. q is zero. An aliquot of solution containing a small amount of chemical substance j is added to a solution held in a thermally insulated container. A rearranged Equation 1.3.4.1 takes the following form.

$$\mathrm{dT} = -\frac{(\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}}{(\partial \mathrm{H}/\partial \mathrm{T})_{\mathrm{p},\xi}} \mathrm{d}\xi \tag{1.3.4.2}$$

Chemical reaction occurs in the sample cell, the rate of chemical reaction being governed by the composition of the solution and appropriate rate constants. The differential isobaric dependence of temperature on time, $\mathrm{dT/dt}$ is given by Equation 1.3.4.3.

$$\frac{\mathrm{dT}}{\mathrm{dt}} = -\frac{(\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}}{(\partial \mathrm{H}/\partial \mathrm{T})_{\mathrm{p},\xi}} \frac{\mathrm{d}\xi}{\mathrm{dt}} \tag{1.3.4.3}$$

The calorimeter records the dependence of temperature on time. An equation based on the Law of Mass Action yields the rate of change of composition $\mathrm{d}\xi/\mathrm{dt}$. The integrated form of Equation 1.3.4.3 yields a calculated dependence of T on time which can be compared with the recorded dependence. This subject is important in the context of **thermal imaging calorimetry** [1-4].

Footnotes

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1.3.5: Calorimetry- Solutions - Heat Flow

At temperature T and pressure p, the enthalpy of a closed system having composition ξ can be defined by Equation 1.3.5.1.[1]

$$\mathrm{H} = \mathrm{H}[\mathrm{T}, \mathrm{p}, \xi] \tag{1.3.5.1}$$

The general differential of Equation 1.3.5.1 takes the following form.

$$\mathrm{dH} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi} \mathrm{dT} + \left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} \mathrm{dp} + \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} \mathrm{d}\xi$$

If the pressure is constant at, for example, ambient pressure, dH equals the differential heat dq passing between system and surroundings. In the application considered here, the temperature is held constant.

The following equation describes heat dq in terms of changes in composition at constant pressure and constant temperature.

Thus

$$\mathrm{dq} = \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} \mathrm{d}\xi$$

Moreover $\mathrm{d}\xi$ is the extent of chemical reaction in the time period dt.

$$\text{Then } \left(\frac{\mathrm{dq}}{\mathrm{dt}}\right) = \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} \left(\frac{\mathrm{d}\xi}{\mathrm{dt}}\right)$$

If the chemical reaction in the sample cell involves a single chemical reaction, $(\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}$ is the enthalpy of reaction $\Delta_{\mathrm{r}}\mathrm{H}$.

$$\text{Therefore, } \left(\frac{\mathrm{dq}}{\mathrm{dt}}\right) = \Delta_{\mathrm{r}}\mathrm{H} \left(\frac{\mathrm{d}\xi}{\mathrm{dt}}\right)$$

In Heat Flow Calorimetry [2,3], a small closed reaction vessel is in contact with a heat sink so that the reaction vessel is held at constant temperature. The flow of heat between sample cell and heat sink is monitored such that the recorded quantity is the **thermal power**, the rate of heat production $(\mathrm{dq}/\mathrm{dt})$ as a result of chemical reaction. The property $(\mathrm{dq}/\mathrm{dt})$ is recorded as a function of time; also as the amount of reactants decreases, $\mathrm{limit}(\mathrm{t} \to \infty)(\mathrm{dq}/\mathrm{dt})$ is zero. Nevertheless because $(\mathrm{d}\xi/\mathrm{dt})$ is a function of time, $(\mathrm{dq}/\mathrm{dt})$ effectively monitors the progress of chemical reaction. Intuitively it is apparent that for an exothermic reaction $(\mathrm{dq}/\mathrm{dt})$ at time zero is also zero, rises rapidly and then decreases to zero as all reactants are consumed.

The Law of Mass Action relates $(\mathrm{d}\xi/\mathrm{dt})$ to the composition of the system at time t. Because $(\mathrm{d}\xi/\mathrm{dt})$ depends on time, $(\mathrm{dq}/\mathrm{dt})$ also depends on time, approaching zero as reactants are consumed.

For example, in the case of a simple chemical reaction of the form $\mathrm{X} \to \mathrm{Y}$ where at $\mathrm{t} = 0$ the amount of chemical substance X is n_{X}^{0}, the amounts of X and Y at time t are $(\mathrm{n}_{\mathrm{X}}^{0} - \xi)$ and ξ moles respectively. If the volume of the sample cell is V,

$$(1/\mathrm{V})\,\mathrm{d}\xi/\mathrm{dt} = (1/\mathrm{V})\,\mathrm{k}\,\left(\mathrm{n}_{\mathrm{X}}^{0} - \xi\right)$$

$$\text{Or,} \quad \mathrm{d}\xi/\mathrm{dt} = \mathrm{k}\,\mathrm{V}\,\left[\mathrm{c}_{\mathrm{x}}^{0} - (\xi/\mathrm{V})\right]$$

$$\text{Or,} \quad \mathrm{d}\xi/\mathrm{dt} = \mathrm{k}\,\mathrm{V}\,\mathrm{c}_{\mathrm{X}}^{0}\,\exp(-\mathrm{k}\,\mathrm{t})$$

Hence using equation (e) and for a dilute solution,

$$\mathrm{dq}/\mathrm{dt} = \Delta_{\mathrm{r}}\mathrm{H}^{0}\,\mathrm{k}\,\mathrm{V}\,\mathrm{c}_{\mathrm{X}}^{0}\,\exp(-\mathrm{k}\,\mathrm{t})$$

The integral of equation (i) between $\mathrm{t} = 0$ and time t yields the amount of heat passing between system and heat sink.[3,4]

$$\text{Thus,} \quad \int_{0}^{\mathrm{t}} \mathrm{dq} = \Delta_{\mathrm{r}}\mathrm{H}^{\circ}\,\mathrm{k}\,\mathrm{V}\,\mathrm{c}_{\mathrm{X}}^{0}\,[1 - \exp(-\mathrm{k}\,\mathrm{t})]$$

Hence the measured dependence of $(\mathrm{dq}/\mathrm{dt})$ is compared with that calculated using equations (i) and (j). The analysis is readily extended to second order reactions. [4,5]

The technique of heat flow calorimetry has been applied across a wide range of subjects (e.g. screening of catalysts [6]and characterising complex reactions[7]) and subject to different analytical approaches.

Footnotes

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1.3.6: Calorimetry - Titration Microcalorimetry

In a common type of calorimeter, aliquots of one liquid (solution or solvent) are injected into a sample cell containing another liquid. The rise in temperature accompanying injection of each aliquot is recorded. The calorimeter is calibrated electrically.

With advances in microelectronics and calorimeter design the volume of liquids required in titration calorimetry has dropped so that only micro-litres of aliquots are injected into a sample cell having a volume of the order $1\ \mathrm{cm}^3$. Operation of the calorimeter is under the control of a mini-computer. The sensitivity of these calorimeters is such that recorded heats are of the order of 10^{-6} J. In a typical experiment sample and reference cells, held in an evacuated enclosure, are heated such that the temperatures of both cells increase at the rate of a few micro-kelvin per second. The electronic heaters and thermistors are coupled so that these temperatures (plus that of the adiabatic shield) stay in step. Under computer control, aliquots of a given solution from a micro-syringe are injected into the sample cell at predetermined intervals. The operation of the calorimeter is readily understood where the chemical processes in the sample cell following injection of an aliquot are exothermic. In this case the temperature of the solution in the sample cell increases so heating of this cell is stopped. The reference cell continues to be heated until at some stage the temperatures of both sample and reference cells are again equal, when again both cells are heated in preparation for the next injection of an aliquot. The computer records how much heat was produced by the electric heaters in the reference cell to recover the situation of equal temperatures. This amount of heat must have been produced effectively by chemical processes in the sample cell.

Titration microcalorimetry [1] has had a major impact in biochemistry with respect to the study of enzyme - substrate binding [2-5].

The starting point of the thermodynamic analysis is the definition of the extensive variable enthalpy H of a closed system in terms of temperature, pressure and composition; equation (a).

$$\mathrm{H} = \mathrm{H}[\mathrm{T}, \mathrm{p}, \xi]$$

The complete differential of equation (a) takes the following form.

$$\mathrm{dH} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi} \mathrm{dT} + \left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} \mathrm{dp} + \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} \mathrm{d}\xi$$

The key term in the present context is the last term in equation (b) which describes a change in enthalpy at constant T and p.

$$\mathrm{dH} = \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} \mathrm{d}\xi$$

In the present context the change in composition/organisation $\mathrm{d}\xi$ refers to the contents of the sample cell accompanying injection of an aliquot from the syringe. Heat q is recorded following injection of $\mathrm{d}n_j{}^0$ moles of chemical substance j into the sample cell on going from injection number I to injection number $\mathrm{I}+1$.

$$\left[\frac{\mathrm{q}}{\mathrm{dn}_\mathrm{j}^0}\right]_1^{1+1} = \left[\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} \frac{\mathrm{d}\xi}{\mathrm{dn}_\mathrm{j}^0}\right]_1^{1+1}$$

Equation (d) is the key to titration microcalorimetry. The recorded quantity q on the left-hand side of equation (d) is the recorded heat at injection number $\mathrm{I}+1$ when further $\mathrm{d}n_j{}^0$ moles of chemical substance j are injected into the sample cell. The right-hand-side shows that the recorded ratio

$$\left[\frac{\mathrm{q}}{\mathrm{dn}_\mathrm{j}^0}\right]_1^{1+1}$$

is related to the dependence of enthalpy H on composition, $\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}}$, and the dependence of composition/organisation on the amount of substance j injected. Plots of $\left[\frac{\mathrm{q}}{\mathrm{dn}_\mathrm{j}^0}\right]_1^{1+1}$ as a function of injection number are called enthalpograms.

Equation (d) highlights an underlying problem in the analysis of experimental results. The recorded quantity is heat q and no information immediately emerges concerning the chemical processes responsible although we note that the sign of heat q is not predetermined; i.e. processes can be exo- or endo- thermic. The r.h.s. of equation (d) involves the product of two quantities,

$\left(\frac{\partial H}{\partial \xi}\right)_{T,p}$ and $\frac{d\xi}{dn_j^0}$. We have no 'a priori' indication concerning how to pull these terms apart. In other words we require a model for the chemical processes in the sample cell.

Footnotes

[1] T. S. Wiseman, S. Williston, J.F.Brandts and Z.-N. Lim, Anal.Biochem., 1979, **179**,131.

[2] Biocalorimetry, ed. J. E. Ladbury and B. Z. Chowdhry, Wiley Chichester, 1998.

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[4] J. Ladbury and B. Z. Chowdhry, Chemistry and Biology, 1996,**3**,79.

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1.3.7: Calorimeter- Titration Microcalorimetry- Enzyme-Substrate Interaction

The technique of titration microcalorimetry was developed with the aim of probing enzyme-substrate interactions.[1,2] At the start of the experiment, the sample cell contains an aqueous solution containing a known amount of a macromolecular enzyme $\mathrm{M(aq)}$. The injected aliquots contain a known amount of substrate X such that during the experiment the composition of the sample cell is described in terms of the following chemical equilibrium.

$$\mathrm{M(aq) + X(aq) \Leftrightarrow MX(aq)}$$

[It is important to note that the term substrate refers to the chemical substance which is bound (adsorbed?) by the macromolecular enzyme. In treatments of adsorption, the macromolecular substrate adsorbs small molecules.] In the limit of strong binding (see below), most of the injected substrate at the start of the experiment is bound by the enzyme. But gradually as more substrate is added, the number of free binding sites decreases until eventually all sites are occupied and hence no heat q is recorded. The plot of $\left[\mathrm{q/dn_X^0}\right]$ against injection number in the textbook case is sigmoidal.

The equilibrium established in the sample cell is described as follows.

	$\mathrm{M(aq)}$	$\mathrm{X(aq)}$ <==>	$\mathrm{MX(aq)}$	
At $\mathrm{t = 0}$	$\mathrm{n^0(M)}$	$\mathrm{n^0(X)}$	0	mol
At $\mathrm{t = \infty}$	$\mathrm{n^0(M) - \xi}$	$\mathrm{n^0(X) - \xi}$	ξ	mol
	$\left[\mathrm{n^0(M) - \xi}\right]\mathrm{/V}$	$\left[\mathrm{n^0(X) - \xi}\right]\mathrm{/V}$	$\xi\mathrm{/V}$	moldm

V is the volume of the sample cell. The analysis uses equilibrium constants defined in terms of the concentrations of chemical substances in the system. There are advantages in using equilibrium constants having the following form where \ (\mathrm{c}_{\mathrm{r} = 1 \mathrm{~mol dm}^{-3}\).

$$\mathrm{K = (\xi/V)\, c_r / \left\{\left[n^0(M) - \xi\right]/V\right\}\left\{\left[n^0(X) - \xi\right]/V\right\}}$$

The latter is a quadratic in the extent of reaction, ξ. [3]

$$\xi^2 + b\,\xi + c = 0$$

where

$$b = -n^0(M) - n^0(X) - V\, c_r\, K^{-1}$$

and

$$\mathrm{c = n^0(M)\, n^0(X)}$$

Therefore

$$\xi = -(b/2) \pm (1/2)\,\left(b^2 - 4\,c\right)^{1/2}$$

The negative root of the quadratic yields the required solution on the grounds that, with increase in $n^0(\mathrm{X}\backslash)$ in the sample cell, more substrate is bound by the enzyme. The required quantity is $\left(\mathrm{d\xi/\, dn_X^0}\right)$. We note that from equations (g) and (h),

$$\mathrm{db/dn_X^0 = -1; \quad dc/dn_X^0 = n_M^0}$$

In the experiment we control the ratio of total amounts of substrate to enzyme, $\mathrm{n^0(X)/n^0(M)}$, which increases as more substrate is added to the sample cell. A measure of the 'tightness of binding' is the fraction of substrate bound when this ratio is unity.

$$\text{By definition,} \quad X_r = n^0(X)/n^0(M) = [X_{\text{total}}]\,/\,[M_{\text{total}}]$$

We define two variables r and C; (note uppercase).

$$\mathrm{V\, c_r/K\, n^0(M) = c_r/K\, [M_{total}] = r = 1/C}$$

$$\text{From equation (e),}\ \mathrm{[X]^{eq}/[MX]^{eq} = c_r/K\, [M]^{eq}}$$

If K is small, then r is large and only a small amount of the injected substrate is bound to the enzyme. $[\mathrm{X}]^{\mathrm{eq}}$ is, in relative terms, large and \([\mathrm{MX}]^{\mathrm{eq}}\) is small. If r is large, C is small.

If on the other hand K is large, r is small, C is large and in the limit all substance X is bound to the enzyme M.

We return to equation (i) because in order to calculate ξ we require b. [4]

$$\mathrm{b}^2 - 4\,\mathrm{c} = \left[\mathrm{n}^0(\mathrm{M})\right]^2\,\left[\mathrm{X}_\mathrm{r}^2 - 2\,\mathrm{X}_\mathrm{r}\,(1-\mathrm{r}) + (1+\mathrm{r})^2\right]$$

We also require $\left[\mathrm{d}\xi/\,\mathrm{dn}^0(\mathrm{X})\right]$ which describes the dependence of extent of substrate binding on total amount of X in the sample cell, noting that we can control the latter through the concentration of the injected aliquots. We return to equation (i) making use of equation (n). [5]

$$\frac{\mathrm{d}\xi}{\mathrm{dn}_\mathrm{X}^0} = \frac{1}{2} + \frac{[1-(1/2)\,(1+\mathrm{r}) - \mathrm{X}_\mathrm{r}/2]}{[\mathrm{X}_\mathrm{r}^2 - 2\,\mathrm{X}_\mathrm{r}\,(1-\mathrm{r}) + (1+\mathrm{r})^2]^{1/2}}$$

The enthalpy of the solution in the sample cell (assuming the thermodynamic properties of the solution are ideal) is given by equation (p).

$$\mathrm{H}(\mathrm{aq};\mathrm{id}) = \mathrm{n}_1(\lambda)\,\mathrm{H}_1^*(\lambda) + \left[\mathrm{n}^0(\mathrm{M}) - \xi\right]\,\mathrm{H}^\infty(\mathrm{M};\mathrm{aq}) + \left[\mathrm{n}_\mathrm{X}^0 - \xi\right]\,\mathrm{H}^\infty(\mathrm{X};\mathrm{aq}) + \xi\,\mathrm{H}^\infty(\mathrm{MX};\mathrm{aq})$$

$$[\partial \mathrm{H}(\mathrm{aq};\mathrm{id})/\partial\xi\xi] = -\mathrm{H}^\infty(\mathrm{M};\mathrm{aq}) - \mathrm{H}^\infty(\mathrm{X};\mathrm{aq}) + \mathrm{H}^\infty(\mathrm{MX};\mathrm{aq}) = \Delta_\mathrm{B}\mathrm{H}^\infty$$

Hence the dependence of the ratio $\left[\mathrm{q}/\mathrm{dn}_\mathrm{X}^0\right]$ on composition of the sample cell is given by equation (r).

$$\frac{\mathrm{q}}{\mathrm{dn}_\mathrm{X}^0} = \Delta_\mathrm{B}\mathrm{H}^\infty\,\left[\frac{1}{2} + \frac{[1-(1/2)\,(1+\mathrm{r}) - \mathrm{X}_\mathrm{r}/2]}{[\mathrm{X}_\mathrm{r}^2 - 2\,\mathrm{X}_\mathrm{r}\,(1-\mathrm{r}) + (1+\mathrm{r})^2]^{1/2}}\right]$$

The latter key equation describes the recorded enthalpogram. The latter falls into one of three general classes determined by the quantity C in equation (λ).

1. $\mathrm{C} = \infty$. All injected substrate is bound to the enzyme over the first few injections such that the ratio $\left[\mathrm{q}/\mathrm{dn}_\mathrm{X}^0\right]$ equals $\Delta_\mathrm{B}\mathrm{H}^\infty$. When all sites are occupied the ratio $\left[\mathrm{q}/\mathrm{dn}_\mathrm{X}^0\right]$ drops to zero and remains at zero for all further injections.
2. $40 < \mathrm{C} < 500$. This is the textbook case where the recorded enthalpogram has a sigmoidal shape. [6] The ratio $\left[\mathrm{q}/\mathrm{dn}_\mathrm{X}^0\right]$ at low injection numbers is close to $\Delta_\mathrm{B}\mathrm{H}^\infty$. The recorded enthalpogram is fitted using a non-linear least squares technique to yield estimates of K and $\Delta_\mathrm{B}\mathrm{H}^\infty$.
3. $0.1 < \mathrm{C} < 20$. Only a small fraction of the injected substrate is bound to the enzyme such that only poor estimates of K and $\Delta_\mathrm{B}\mathrm{H}^\infty$ are obtained.

Footnotes

[1] T. S. Wiseman, S. Williston, J.F.Brandts and Z.-N. Lim, Anal. Biochem., 1979,**179**,131.

[2] M. J. Blandamer, in Biocalorimetry, ed. J. E. Ladbury and B. Z. Chowdhry, Wiley Chichester, 1998, p5.

[3] $\mathrm{n}^0(\mathrm{M})\,\mathrm{n}^0(\mathrm{X}) - \xi\,\left[\mathrm{n}^0(\mathrm{M}) + \mathrm{n}^0(\mathrm{X})\right] + \xi^2 = \mathrm{V}\,\mathrm{c}_\mathrm{r}\,\mathrm{K}^{-1}\,\xi$

[4]

$$b^2 = \left[-n^0(M) - n^0(X) - V\,c_r\,K^{-1}\right]^2$$

$$\text{or, } b^2 = \left[n^0(M)\right]^2\,\left[1 + n^0(X)/n^0(M) + V\,c_r/K\,n^0(M)\right]^2$$

$$\mathrm{b}^2 - 4\,\mathrm{c} = \left[\mathrm{n}^0(\mathrm{M})\right]^2\,\left[\mathrm{n}^0(\mathrm{X})/\mathrm{n}^0(\mathrm{M}) + 1 + \mathrm{V}\,\mathrm{c}_\mathrm{r}/\mathrm{K}\,\mathrm{n}^0(\mathrm{M})\right]^2 - 4\,\mathrm{n}^0(\mathrm{M})\,\mathrm{n}^0(\mathrm{X})$$

$$\text{Or, } b^2 - 4\,c = \left[n^0(M)\right]^2\,\left[X_r + 1 + r\right]^2 - 4\,n^0(M)\,n^0(X)$$

$$\mathrm{b}^2 - 4\,\mathrm{c} = \left[\mathrm{n}^0(\mathrm{M})\right]^2\,\left[(\mathrm{X}_\mathrm{r}+1)^2 + \mathrm{r}^2 + 2\,\mathrm{r}\,(\mathrm{X}_\mathrm{r}+1)\right] - 4\,\mathrm{n}^0(\mathrm{M})\,\mathrm{n}^0(\mathrm{X})$$

$$b^2 - 4\,c = \left[n^0(M)\right]^2\ \left[X_r^2 + 2\,X_r + 1 + r^2 + 2\,r\,X_r + 2\,r - 4\,X_r\right]$$

[5] From equation (i)

$$\frac{d\xi}{dn_x^0} = -\frac{1}{2}\frac{db}{dn_x^0} - \frac{1}{2}\,\frac{1}{2}\,\frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,\left[2\,b\,\frac{db}{dn_x^0} - 4\,\frac{dc}{dn_x^0}\right]$$

$$\text{Or,}\quad \frac{d\xi}{dn_X^0} = -\frac{1}{2}\frac{db}{dn_X^0} - \frac{1}{2}\,\frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,\left[b\,\frac{db}{dn_X^0} - 2\,\frac{dc}{dn_X^0}\right]$$

We ignore for the moment the term $(b^2 - 4\,c)^{1/2}$ and concentrate attention on the two derivatives $\frac{db}{dn_X^0}$ and $\frac{dc}{dn_X^0}$; equation (j).

$$\frac{d\xi}{dn_X^0} = \frac{1}{2} - \frac{1}{2}\,\frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,\left[-1\,\left\{-n^0(M) - n^0(X) - V\,c_r\,K^{-1}\right\} - 2\,n^0(M)\right]$$

$$\text{Or,}\ \frac{d\xi}{dn_X^0} = \frac{1}{2} + \frac{1}{2}\,\frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,\left[n^0(M) - n^0(X) - V\,c_r\,K^{-1}\right]$$

$$\text{Or,}\quad \frac{d\xi}{dn_X^0} = \frac{1}{2} + \frac{1}{2}\,\frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,n^0(M)\,\left[1 - n^0(X)/n^0(M) - V\,c_r/K\,n^0(M)\right]$$

$$\text{Or,}\quad \frac{d\xi}{dn_x^0} = \frac{1}{2} + \frac{1}{2}\,\frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,n^0(M)\,\left[2 - \left\{1 + V\,c_r/K\,n^0(M)\right\} - n^0(X)/n^0(M)\right]$$

$$\text{Or}\quad \frac{d\xi}{dn_X^0} = \frac{1}{2} + \frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,n^0(M)\,\left[1 - (1/2)\,\left\{1 + V\,c_r/K\,n^0(M)\right\} - \left\{n^0(X)/2\,n^0(M)\right\}\right]$$

Now consider the term $(b^2 - 4\,c)^{1/2}$. From equation (n)

$$b^2 - 4\,c = \left[n^0(M)\right]^2\ \left[X_r^2 - 2\,X_r\,(1 - r) + (1 + r)^2\right]$$

$$\text{But}\ \frac{d\xi}{dn_x^0} = \frac{1}{2} + \frac{1}{\left(\,b^2 - 4\,c\right)^{1/2}}\,n^0(M)\,\left[1 - (1/2)\,(1 + r) - X_r/2\right]$$

[6] J. E. Ladbury and B. Z.Chowdhry, Chemistry and Biology, 1996, **3**, 791.

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1.3.8: Calorimetry- Titration Microcalorimetry- Micelle Deaggregation

Aliquots of a concentrated surfactant solution are injected into the sample cell of a titration microcalorimeter. The sample cell initially contains water(λ). As more surfactant solution is injected into the sample cell a stage is reached where the concentration of surfactant in the sample cells exceeds the critical micellar concentration, cmc. The magnitude of the recorded heat changes dramatically, leading to estimates of both the cmc and the enthalpy of micelle formation.

This calorimetric techniques has proved important in studies of ionic surfactants; e.g. hexadecyltrimethylammonium bromide (CTAB). For these surfactants the microcalorimeter signals a marked difference in recorded heats as the concentration of the surfactant changes from below to above the cmc. Titration microcalorimetric results for non-ionic surfactants are unfortunately not so readily interpreted. In addition to micelle formation, the monomers cluster in small aggregates below the cmc and the micelles cluster above the cmc.

Analysis

The volume of injected aliquot vinj is significantly less than the volume of the sample cell. The amount of surfactant in each aliquot is ninj, the concentration of surfactant being $\mathrm{cinj}[=\mathrm{ninj}/\ \mathrm{vinj}\ ]$. If cinj is significantly above the cmc, the contribution of the surfactant to the enthalpy of the injected aliquot is $\mathrm{ninj}\ \mathrm{H_j^0(mic)}$ where $\mathrm{H_j^0(mic)}$ is the contribution of one mole of monomer to the molar enthalpy of a micelle. If the concentration of solution in the sample cell is below the cmc, the contribution of each monomer to the enthalpy of the solution equals $\mathrm{H_j^0(\ mon\ )}$. We concentrate attention on the contribution of the surfactant to the enthalpies of injected solution and the solution in the sample cell.

Enthalpy of the injected aliquot,

$$\mathrm{H(inj)} = \mathrm{ninj}\ \mathrm{H_j^0(mic)}$$

The contribution of the surfactant to the enthalpy of the solution in the sample cell at injection number I is given by equation (b).

Enthalpy of solution in the sample cell at injection number I,

$$\mathrm{H(I)} = \mathrm{I}\ \mathrm{ninj}\ \mathrm{H_j^0}\ \mathrm{(mon)}$$

Enthalpy of solution in the sample cell at injection number (I+1),

$$\mathrm{H(I+1)} = \mathrm{(I+1)}\ \mathrm{ninj}\ \mathrm{H_j^0}\ \mathrm{(mon)}$$

Recorded heat

$$\mathrm{q} = \mathrm{H(!+1)} - \mathrm{H(I)} - \mathrm{H(\ inj\ )}$$

$$\mathrm{or,}\ [\mathrm{q}/\ \mathrm{ninj}\ ]_{\mathrm{lowl}}\ = \mathrm{H_j^0(mon)} - \mathrm{H_j^0(mic)} = -\Delta_{\mathrm{mic}}\ \mathrm{H^0}$$

At high injection numbers the enthalpies of solution in the sample cell are $\mathrm{I}\ \mathrm{ninj}\ \mathrm{H_j^0(mic)}$ and $\mathrm{(I+1)}\ \mathrm{ninj}\ \mathrm{H_j^0(mic)}$.

$$[\mathrm{q}/\ \mathrm{ninj}\ ]_{\mathrm{highl}}\ = \mathrm{(I+1)\,H_j^0(mic)} - \mathrm{I\,H_j^0(\ mic\ )} - \mathrm{H_j^0(\ mic\ )} = 0$$

At low injection numbers the recorded $(q/\ \mathrm{ninj})$ is effectively the enthalpy of micelle formation. The recorded ratio $[q/\ \mathrm{ninj}]$ is effectively zero at high injection numbers, the switch in pattern of $(q/\ \mathrm{ninj})$ from $\Delta_{\mathrm{mic}}\mathrm{H^0}$ to zero marking the cmc of the surfactant.

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1.3.9: Calorimetry- Scanning

A given closed system is prepared using n_1 moles of water (λ) and n_X^0 moles of solute X at pressure p ($\cong p^0$, the standard pressure) and temperature T. The thermodynamic properties of the solution are ideal such that, at some low temperature, the enthalpy of the solution $H(aq;\ low\ T)$ is given by equation (a).

$$H(aq;\ low\ T) = n_1\, H_1^*(\lambda;\ low\ T) + n_X^0\, H_X^\infty(\ aq\ ;\ low\ T)$$

The temperature of the solution is raised to high temperature such that the solution contains only solute Y, all solute X having been converted to Y.

$$H(aq;\ high\ T) = n_1\, H_1^*(\lambda;\ high\ T) + n_X^0\, H_Y^\infty(\ aq;\ high\ T)$$

At intermediate temperatures, a chemical equilibrium exists between solutes X and Y. At temperature T, the chemical composition of the solution is characterised by extent of reaction $\xi(T)$.

	X(aq) <=	Y(aq)	
At low T	n_X^0	0	mol
At high T	0	n_x^0	mol
At intermediate T	$n_X^0 - \xi^{eq}(T)$	$\xi^{eq}(T)$	mol

For a solution where the thermodynamic properties are ideal, we define an equilibrium constant K(T), at temperature T.

$$K(T) = \xi^{eq}(T) / \left[n_X^0 - \xi^{eq}(T)\right]$$

By definition, the degree of reaction, $\alpha(T) = \xi^{eq}(T)/n_x^0$.

$$K(T) = \alpha(T)\, n_X^0 / \left[n_X^0 - n_X^0\, \alpha(T)\right]$$

$$\text{Therefore,}\quad \alpha(T) = K(T)/[1 + K(T)]$$

At temperature T, the enthalpy of the aqueous solution is given by equation (f) where $H_1^*(\lambda; T)$ is the molar enthalpy of water(λ) in the aqueous solution again assuming that the thermodynamic properties of the solution are ideal.

$$H(aq; T) = n_1\, H_1^*(\lambda; T) + n_X^0\, [1 - \alpha(T)]\, H_X^\infty(aq; T) + n_X^0\, \alpha(T)\, H_Y^0(aq; T)$$

The limiting enthalpy of reaction, $\Delta_r H^\infty(aq; T)$ is given by equation (g).

$$\Delta_r H^\infty(aq; T) = H_Y^\infty(aq; T) - H_X^\infty(aq; T)$$

From equation (f),

$$H(aq; T) = n_1\, H_1^*(\lambda; T) + n_X^0\, H_X^\infty(aq; T) + n_x^0\, \alpha(T)\, \Delta_r H^\infty(aq; T)$$

We assume that $\Delta_r H^\infty(aq)$ is independent of temperature. The differential of equation (h) with respect to temperature yields the isobaric heat capacity of the solution.

$$C_p(aq) = n_1\, C_{p1}^*(\lambda) + n_X^0\, C_{pX}^\infty(aq) + n_X^0\, \Delta_r H^\infty(aq)\, d\alpha/dT$$

The term $(d\alpha/dT)$ signals the contribution of the change of composition with temperature to the isobaric heat capacity of the system, the 'relaxational' isobaric heat capacity $C_p(relax)$.

Thus

$$C_p(\ relax\ ) = n_X^0\, \Delta_r H^\infty(aq)\, d\alpha/dT$$

$$\text{From equation (e)[1]}\quad \frac{d\alpha(T)}{dT} = \frac{K(T)}{[1 + K(T)]^2}\, \frac{d\ln[K(T)]}{dT}$$

But according to the van't Hoff Equation,

$$\frac{\mathrm{d}\ln \mathrm{K(T)}}{\mathrm{dT}} = \frac{\Delta_{\mathrm{r}}\mathrm{H}^{\infty}}{\mathrm{R\,T}^2}$$

$$\text{Hence [2], } \mathrm{C_p(\ relax\ )} = \mathrm{n_x^0}\,\frac{\left[\Delta_{\mathrm{r}}\mathrm{H}^{\infty}(\mathrm{aq})\right]^2}{\mathrm{R\,T}^2}\,\frac{\mathrm{K(T)}}{[1+\mathrm{K(T)}]^2}$$

The contribution to the molar isobaric heat capacity of the system from the change in composition of the solution is given by equation (n).

$$C_{pm}(\ \mathrm{relax}\ ) = \frac{\left[\Delta_{\mathrm{r}}\mathrm{H}^{\infty}(\mathrm{aq})\right]^2}{\mathrm{R\,T}^2}\,\frac{\mathrm{K(T)}}{[1+\mathrm{K(T)}]^2}$$

The dependence of $C_{pm}(\mathrm{relax})$ on temperature has the following characteristics.

i. The plot forms a bell-shaped curve such that at very low and very high temperatures, $(C_{pm}(\mathrm{relax})$ is zero [3-5].
ii. $(C_{pm}(\mathrm{max})$ occurs at the temperature T_m.
iii. The area under the 'bell' equals the enthalpy of reaction [6,7]. A scanning calorimeter is designed to raise the temperature of a sample (solution) in a controlled fashion. The calorimeter uses controlled electrical heating while monitoring the temperatures of a sample cell and a reference cell containing just solvent. If the heat capacity of the cell containing the sample under investigation starts to increase the calorimeter records the fact that more electrical energy is required to raise the temperature of the sample cell by say $0.1\ \mathrm{K}$ than required by the reference.

The tertiary structures of enzymes in aqueous solution are very sensitive to temperature. In the general case, an enzyme changes from, say, active to inactive form as the temperature is raised; i.e. the enzyme denatures. The change from active to inactive form is characterised by a 'melting temperature'. The explanation is centred on the role of hydrophobic interactions in stabilising the structure of the active form. However the strength of hydrophobic bonding is very sensitive to temperature. Hence equation (n) forms the basis of an important application of modern differential scanning calorimeters [3] into structural reorganisation in biopolymers on changing the temperature [4-7]. The scans may also identify domains within a given biopolymer which undergo structural transitions at different temperatures [8].

Indeed there is evidence that a given enzyme is characterised by a temperature range within which the active form is stable. Outside this range, both at low and high temperatures the active form is not stable. In other words the structure of an enzyme may change to an inactive form on lowering the temperature [9,10]. The pattern can be understood in terms of the dependence of $\left[\mu_{\mathrm{j}}^0/\mathrm{T}\right]$ on temperature where Extra \left or missing \right is the reference chemical potentials for solute j. In this case we consider the case where in turn solute j represents the active and inactive forms of the enzyme. There is a strong possibility that the plots of two dependences intersect at two temperatures. The active form is stable in the window between the two temperatures.

The analysis leading to equation (n) is readily extended to systems involving coupled equilibria [11,12]. The impact of changes in composition is also an important consideration in analysing the dependence on temperature of the properties of weak acids in solution [13- 15].

Footnotes

[1] $$\frac{\mathrm{d}\alpha}{\mathrm{dT}} = \left[\frac{1}{1+\mathrm{K}} - \frac{1}{(1+\mathrm{K})^2}\right]\frac{\mathrm{dK}}{\mathrm{dT}} = \left[\frac{1+\mathrm{K}-\mathrm{K}}{(1+\mathrm{K})^2}\right]\frac{\mathrm{dK}}{\mathrm{dT}} = \left[\frac{1}{(1+\mathrm{K})^2}\right]\frac{\mathrm{dK}}{\mathrm{dT}} = \left[\frac{\mathrm{K}}{(1+\mathrm{K})^2}\right]\frac{\mathrm{d}\ln \mathrm{K}}{\mathrm{dT}}$$

[2] $$\mathrm{C_p(\ relax\ )} = [\mathrm{mol}]\,\frac{\left[\mathrm{Jmol^{-1}}\right]^2}{\left[\ \mathrm{J\ K^{-1}\ mol^{-1}}\right]\ [\mathrm{K}]^2}\,\frac{[1]}{[1]} = [\mathrm{JK^{-1}}]$$

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1.3.10: Calorimetry- Solutions- Flow Microcalorimetry

An important event in experimental calorimetry was the development of the Picker flow microcalorimeter [1-3]. In this calorimeter, two liquids [e.g. water(λ) and an aqueous solution] at the same temperature flow through two cells. The liquids are heated, the calorimeter recording the difference in power required to keep both liquids at the same temperature. The recorded difference is a function of the difference in isobaric heat capacities per unit volume. The isobaric heat capacity of the solvent [e.g. water(λ)] per unit volume (or, heat capacitance) , $\sigma^*(\lambda)$ is the reference. The technique has been extended to measure enthalpies and rates of reaction [4].

Footnotes

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1.4.1: Chemical Equilibria- Solutions

The conditions for chemical equilibrium in a closed system [1,2] at fixed temperature and pressure are as follows.

i. Minimum in Gibbs energy.
ii. Affinity for spontaneous change, A equals zero.
iii. Rate of chemical reaction, $\mathrm{d}\xi/\mathrm{dt} = 0$.
iv. For a chemical equilibrium involving i-chemical substances, the equilibrium chemical potentials of all substances in the system conform to the following condition.

$$\sum_{j=1}^{j=i} v_j \, \mu_j^{eq} = 0$$

If all i-chemical substances are solutes in aqueous solution at temperature T and pressure p, the latter being close to the standard pressure p^0, the equilibrium chemical potentials are related to the composition of the system [3]. Hence,

$$A^{\mathrm{eq}} = -\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{\mathrm{T,p}}^{\mathrm{eq}} = 0 = -\sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{v_j} \, \left[\mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^0\right)\right]^{\mathrm{eq}}$$

\text { Hence } \quad \sum_{j=1}^{j=i} v_{j} \, \mu_{j}^{0}(a q)=-\sum_{j=1}^{j=i} v_{j} \, R \, T \, \ln \left(m_{j} \, \gamma_{j} / m^{0}\right)^{e q} \nonumber \]

The left-hand-side of equation (c) defines the standard Gibbs energy of reaction, $\Delta_{\mathrm{r}}\mathrm{G}^0$ which in turn leads to the definition of an equilibrium constant K^0.[1]

$$\Delta_{\mathrm{r}}\mathrm{G}^0 = -\mathrm{R\,T\,ln}\left(\mathrm{K}^0\right) = \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{v_j}\,\mu_{\mathrm{j}}^{0}(\mathrm{aq})$$

Combination of equation (c) and equation (d) yields an equation for K^0 in terms of the equilibrium composition of the system [3].

$$\mathrm{K}^0 = \left[\Pi_{\mathrm{j=1}}^{\mathrm{j=i}} \left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^0\right)^{\mathrm{v(j)}}\right]^{\mathrm{eq}}$$

Equation (e) is remarkable. The right hand side describes the stoichiometry of the chemical equilibrium and the composition of the closed system at defined temperature and pressure. The left-hand-side in the form of K^0 defined using equation (d) is related to the ideal thermodynamic process in terms of reference chemical potentials of reactants and products. If the solutes are non-ionic and the solution is dilute then a reasonable assumption sets $''\gamma_j^{eq} = 1''$ for all i-solutes.

Footnotes

[1] From a thermodynamic standpoint, an equilibrium constant emerges from the idea of zero affinity for chemical reaction at a minimum in Gibbs energy. Accounts which treat equilibrium constants as the ratio of rate constants are unsatisfactory.

[2] The equations set out here describe the general case where substance j is one of i-simple solutes in solution. In some cases one or more of the solutes are ionic and the solvent (e.g. water) is directly involved in the chemical reaction. In each case we assume that the systems have been assayed such that the composition of the system at equilibrium is known together with the stoichiometries.

[3] In general terms for a systems at pressure p,

$$\mathrm{A}^{\mathrm{eq}} = -\left(\frac{\partial G}{\partial \xi}\right)_{\mathrm{T,p}}^{\mathrm{eq}} = 0$$

Hence for a chemical equilibrium involving i-solutes in aqueous solution the following condition holds.

$$0 = \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{v_j} \left[\mu_{\mathrm{j}}^{0}\left(\mathrm{aq;T;p}^0\right) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^0\right) + \int_{\mathrm{p}^0}^{p} \mathrm{V_j^{\infty}(aq)\,dp}\right]^{\mathrm{eq}}$$

$$\sum_{j=1}^{j=i} v_j \, \mu_j^0 \left(aq; T; p^0 \right) = - \sum_{j=1}^{j=i} v_j \left[R \, T \, \ln \left(m_j \, \gamma_j / m^0 \right) + \int_{p^0}^{p} V_j^{\infty} (aq) \, dp \right]^{eq}$$

$$\text{where } \Delta_r G^0 \left(\, T; p^0 \right) = - R \, T \, \ln \left(K^0 \right) = \sum_{j=1}^{j=i} v_j \, \mu_j^0 \left(aq; T; p^0 \right)$$

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1.4.2: Chemical Equilibria- Solutions- Derived Thermodynamic Parameters

A given closed system at fixed temperature and fixed pressure contains a number of chemical substances in chemical equilibrium. The composition of the system depends on temperature and pressure. Key equations describe the dependences of the equilibrium Gibbs energy on temperature and pressure. $H^{eq} = -T^2 \left(\frac{\partial (G/T)}{\partial T}\right)_p^{eq}$; $V^{eq} = \left(\frac{\partial G}{\partial p}\right)_T^{eq}$ The situation is complicated by the fact that both H^{eq} and V^{eq} depend on the equilibrium composition of the system, ξ^{eq}; $\left(\frac{\partial H}{\partial \xi}\right)_{T,p}^{eq}$ and $\left(\frac{\partial V}{\partial \xi}\right)_{T,p}^{eq}$. We consider the case where the chemical substances involved in the chemical equilibrium are solutes. Both partial derivatives are re-expressed in terms of the partial molar properties of each solute in the system.

\[\left(\frac{\partial H}{\partial \xi}\right)_{T, p}^{e q}=\sum_{j=1}^{j=i}\left(\frac{\partial H}{\partial n_{j}}\right)_{T, p, n(i \neq j)}^{e q} \,\left(\frac{\partial n_{j}}{\partial \xi}\right)^{e q}]

$$\text{But partial molar enthalpy,} \quad H_j^{eq} = \left(\frac{\partial H}{\partial n_j}\right)_{T,p,n(i\neq j)}^{eq}$$

$$\text{Further,} \quad (\partial n_j/\partial \xi)^{eq} = v_j$$

Here ν_j is the stoichiometry associated with chemical substance j, being positive for products and negative for reactants.

$$\text{Therefore,} \quad \left(\frac{\partial H}{\partial \xi}\right)_{T,p}^{eq} = \sum_{j=1}^{j=i} v_j H_j^{eq}$$

$$\text{Therefore,} \quad \left(\frac{\partial V}{\partial \xi}\right)_{T,p}^{eq} = \sum_{j=1}^{j=i} V_j V_j^{eq}$$

V_j^{eq} is the partial molar volume of substance j in the solution at equilibrium. The partial molar enthalpy of solute j can be expressed in terms of a limiting molar enthalpy H_j^{∞} and the dependence of activity coefficient γ_j on temperature.

$$\text{Therefore,} \quad \left(\frac{\partial H}{\partial \xi}\right)_{T,p}^{eq} = \sum_{j=1}^{j=i} v_j \left[H_j^{\infty} - R T^2 \left(\frac{\partial \ln(\gamma_j)}{\partial T}\right)_p^{eq}\right]$$

In other words the dependence of enthalpy of the system on composition at equilibrium is a function of the limiting molar enthalpies of all chemical substances involved in the equilibrium and the dependences on temperature of their activity coefficients.

By definition, the limiting molar enthalpy of reaction,

$$\Delta_r H^{\infty} = \sum_{j=1}^{j=i} v_j H_j^{\infty}$$

$$\text{Then [1]} \quad \left(\frac{\partial H}{\partial \xi}\right)_{T,p}^{eq} = \Delta_r H^{\infty} - \sum_{j=1}^{j=i} v_j R T^2 \left(\frac{\partial \ln \gamma_j}{\partial T}\right)_p^{eq}$$

In some applications, the solutions are quite dilute and the assumption is made that at all temperatures and pressures γ_j for chemical substance j is unity.

$$\text{Hence,} \quad \left(\frac{\partial H}{\partial \xi}\right)_{T,p}^{eq} = \Delta_r H^{\infty}$$

A similar analysis is possible in terms of partial molar volumes. From equation (e), we obtain the following equation for the volume of reaction.

$$\left(\frac{\partial V}{\partial \xi}\right)_{T,p}^{eq} = \sum_{j=1}^{j=i} V_j \left[V_j^{\infty} + R T \left(\frac{\partial \ln(\gamma_j)}{\partial p}\right)_T^{eq}\right]$$

$$\text{The limiting volume of reaction,} \ \Delta_r V^{\infty} = \sum_{j=1}^{j=i} v_j V_j^{\infty}$$

Thus [2], $$\left(\frac{\partial V}{\partial \xi}\right)_{T,p}^{eq} = \Delta_r V^{\infty} + \sum_{j=1}^{j=i} v_j \, R \, T \left(\frac{\partial \ln(\gamma_j)}{\partial p}\right)_T^{eq}$$

If the solution is dilute, it can often be assumed that the activity coefficient of each chemical substance is independent of pressure. Then,

$$\left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}}^{\mathrm{eq}} = \Delta_{\mathrm{r}} \mathrm{V}^{\infty}$$

A slight complication to these general equations arises if one of the substances involved in the chemical equilibrium is the solvent. As an example we consider the following equilibrium.

$$\mathrm{X(aq)} + \mathrm{H_2O(aq)} \rightleftharpoons \mathrm{Y(aq)}$$

$$\begin{aligned}\text{Then,}\quad (\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}^{\mathrm{eq}} &= \left[\mathrm{H}_{\mathrm{Y}}^{\infty}(\mathrm{aq}) - \mathrm{R\,T}^2 \, (\partial \ln \gamma_{\mathrm{Y}}/\partial \mathrm{T})_{\mathrm{p}}^{\mathrm{eq}}\right] \\ &- \left[\mathrm{H}_{\mathrm{X}}^{\infty}(\mathrm{aq}) - \mathrm{R\,T}^2 \, (\partial \ln \gamma_{\mathrm{X}}/\partial \mathrm{T})_{\mathrm{p}}^{\mathrm{eq}}\right] \\ &- \left[\mathrm{H}_1^{*}(\lambda) + \mathrm{R\,T}^2 \, \mathrm{M}_1 \, (\, \mathrm{m_X} + \mathrm{m_Y})_{\mathrm{p}}^{\mathrm{eq}} \, (\partial \phi/\partial \mathrm{T})_{\mathrm{p}}^{\mathrm{eq}}\right]\end{aligned}$$

If the properties of the solution are ideal (e.g. very dilute), equation (o) is written in the following form.

$$(\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}^{\mathrm{eq}} = \mathrm{H}_{\mathrm{Y}}^{\infty}(\mathrm{aq}) - \mathrm{H}_{\mathrm{X}}^{\infty}(\mathrm{aq}) - \mathrm{H}_1^{*}(\lambda)$$

With reference to the limiting volume of reaction, the analogue of equation (p) is as follows.

$$(\partial \mathrm{V}/\partial \xi)_{\mathrm{T,p}}^{\mathrm{eq}} = \mathrm{V}_{\mathrm{Y}}^{\infty}(\mathrm{aq}) - \mathrm{V}_{\mathrm{X}}^{\infty}(\mathrm{aq}) - \mathrm{V}_1^{*}(\lambda)$$

Footnotes

[1] $\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} = \left[\mathrm{Jmol^{-1}}\right] + \left[[1] \; \left[\mathrm{JK^{-1}\ mol^{-1}}\right] \; [\mathrm{K}]^2 \; \left(\frac{[1]}{[\mathrm{K}]}\right)\right] = \left[\mathrm{Jmol^{-1}}\right]$

[2] $\left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}} = \left[\mathrm{m^3\ mol^{-1}}\right] + \left[[1] \; \left[\mathrm{JK^{-1}\ mol^{-1}}\right] \; [\mathrm{K}] \; \left[\frac{[1]}{[\mathrm{Nm^{-2}}]}\right]\right] = \left[\mathrm{m^3\ mol^{-1}}\right]$

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1.4.3: Chemical Equilibria- Solutions- Simple Solutes

A given chemical equilibrium involves association of two solutes $\mathrm{X(aq)}$ and $\mathrm{Y(aq)}$ to form solute $\mathrm{Z(aq)}$.

$$2X(aq) + Y(aq) \rightleftharpoons 4Z(aq)$$

Phase Rule. The aqueous solution is prepared using two chemical substances: substance Z and solvent water. Hence $\mathrm{C} = 2$. There are 2 phases: vapour and solution so $\mathrm{P} = 2$. Then $\mathrm{F} = 2$. Hence at fixed temperature and in a system prepared using mole fraction x_{Z} of substance Z (an intensive composition variable), the equilibrium vapour pressure and the equilibrium amounts of $\mathrm{X(aq)}$, $\mathrm{Y(aq)}$ and $\mathrm{Z(aq)}$ are unique.

$$\text{At equilibrium, } 2\,\mu_{\mathrm{X}}^{\mathrm{eq}}(\mathrm{aq}) + \mu_{\mathrm{Y}}^{\mathrm{eq}}(\mathrm{aq}) = 4\,\mu_{\mathrm{Z}}^{\mathrm{eq}}(\mathrm{aq})$$

At fixed T and p, assuming ambient pressure is close to the standard pressure p^0,

$$\begin{aligned} 2\,&\left[\mu_{\mathrm{X}}^{0}(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_X}\,\gamma_{\mathrm{X}}/\mathrm{m}^0\right)^{\mathrm{eq}}\right] \\ &+ \left[\mu_{\mathrm{Y}}^{0}(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_Y}\,\gamma_{\mathrm{Y}}/\mathrm{m}^0\right)^{\mathrm{eq}}\right] \\ &= 4\,\left[\mu_{\mathrm{Z}}^{0}(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_Z}\,\gamma_{\mathrm{Z}}/\mathrm{m}^0\right)^{\mathrm{eq}}\right] \end{aligned}$$

$$\text{where } \Delta_{\mathrm{r}}\mathrm{G}^0 = -\mathrm{R\,T\,ln}\left(\mathrm{K}^0\right) = 4\,\mu_{\mathrm{Z}}^{0}(\mathrm{aq}) - 2\,\mu_{\mathrm{X}}^{0}(\mathrm{aq}) - \mu_{\mathrm{Y}}^{0}(\mathrm{aq})$$

For this equilibrium at temperature T and pressure p,

$$\mathrm{K}^0 = \frac{\left(\mathrm{m}_{\mathrm{Z}}^{\mathrm{eq}}\,\gamma_{\mathrm{Z}}^{\mathrm{eq}}/\mathrm{m}^0\right)^4}{\left(\mathrm{m}_{\mathrm{X}}^{\mathrm{eq}}\,\gamma_{\mathrm{X}}^{\mathrm{eq}}/\mathrm{m}^0\right)^2\,\left(\mathrm{m}_{\mathrm{Y}}^{\mathrm{eq}}\,\gamma_{\mathrm{Y}}^{\mathrm{eq}}/\mathrm{m}^0\right)}$$

If the solution is quite dilute, $\gamma_{\mathrm{X}}^{\mathrm{eq}}$, $\gamma_{\mathrm{Y}}^{\mathrm{eq}}$ and \gamma_{\mathrm{Z}}^{\mathrm{eq}} are effectively unity in the real solution at equilibrium. Then

$$\mathrm{K}^0 = \left(\mathrm{m}_{\mathrm{eq}}^{\mathrm{eq}}/\mathrm{m}^0\right)^4 / \left(\mathrm{m}_{\mathrm{X}}^{\mathrm{eq}}/\mathrm{m}^0\right)^2\,\left(\mathrm{m}_{\mathrm{Y}}^{\mathrm{eq}}/\mathrm{m}^0\right)$$

K^0 is dimensionless. But the latter statement signals a common problem in this subject because chemists find it more convenient and informative to define a quantity ${\mathrm{K_m}}^0$ in which the m0 terms in equation (f) [or its equivalent] have been removed.

$$\text{Thus, } \mathrm{K}_{\mathrm{m}}^0 = \left(\mathrm{m}_{\mathrm{Z}}^{\mathrm{eq}}\right)^4 / \left(\mathrm{m}_{\mathrm{X}}^{\mathrm{eq}}\right)^2\,\left(\mathrm{m}_{\mathrm{Y}}^{\mathrm{eq}}\right)$$

Hence the units for ${\mathrm{K_m}}^0$ signal the stoichiometry of the equilibrium whereas the dimensionless K^0 does not [1,2].

Footnotes

[1] As a consequence of the removal of the m^0 terms, K^0 quantities have units unless the equation for the chemical equilibrium is stoichiometrically balanced: e.g. n-moles of reactants form n-moles of products.

But from equation (g), $\mathrm{K}_{\mathrm{m}}^0 = \left[\mathrm{molkg}^{-1}\right]^4\,\left[\mathrm{molkg}^{-1}\right]^{-2}\,\left[\mathrm{molkg}^{-1}\right]^{-1}$ or $\mathrm{K}_{\mathrm{m}}^0 = \left[\mathrm{molkg}^{-1}\right]$

If we write, $\Delta_{\mathrm{r}}\mathrm{G}^0 = -\mathrm{R\,T\,ln}\left(\mathrm{K}_{\mathrm{m}}^0\right)$

Then $\Delta_{\mathrm{r}}\mathrm{G}^0 = \left[\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}\right]\,[\mathrm{K}]\,\ln\left[\mathrm{molkg}^{-1}\right]$

ln There is clearly a slight problem in handling a logarithm of a composition unit. There are two approaches to this problem. The first approach ignores the problem, which is unsatisfactory practice. The second approach is to ask - what happened to the composition unit and trace the problem back through the equations.

[2] The impact of composition units in quantitative analysis of data was addressed by E. A. Guggenheim, Trans. Faraday Soc., 1937,**33**,607.

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1.4.4: Chemical Equilibria- Solutions- Ion Association

A given equilibrium in aqueous solution involves association of two ions to form a neutral solute.

$$\text{Thus,} \quad \mathrm{M^+(aq) + X^-(aq) \rightleftharpoons Z(aq)}$$

The chemical equilibrium is described in terms of chemical potentials using the following equation in which we recognise that the reactant is a 1:1 salt.

$$\mu^0\left(\mathrm{M^+X^-;aq}\right) + 2\,\mathrm{R\,T}\,\ln\left[\mathrm{m}\left(\mathrm{M^+X^-}\right)\,\gamma_\pm\left(\mathrm{M^+X^-}\right)/\mathrm{m^0}\right]^{\mathrm{eq}} = \mu^0(Z;\mathrm{aq}) + \mathrm{R\,T}\,\ln\left[\mathrm{m(Z)}\,\gamma(\mathrm{Z})/\mathrm{m^0}\right]^{\mathrm{cq}}$$

In the latter equation, $\gamma_\pm\left(\mathrm{M^+X^-}\right)$ is the mean ionic activity for salt $\mathrm{M^+X^-}$ in the aqueous solution.

By definition, at fixed temperature T and pressure p where this pressure is ambient and hence close to the standard pressure p^0,

$$\Delta_\mathrm{r}\mathrm{G}^0 = \mu^0(\mathrm{Z;aq}) - \mu^0\left(\mathrm{M^+X^-;aq}\right) = -\mathrm{R\,T}\,\ln\mathrm{K}^0$$

where,

$$\mathrm{K}^0 = \left[\frac{\mathrm{m(Z)}\,\gamma(\mathrm{Z})/\mathrm{m}^0}{\mathrm{m}^2\left(\mathrm{M^+X^-}\right)\,\gamma_\pm^2\left(\mathrm{M^+X^-}\right)/\left(\mathrm{m}^0\right)^2}\right]^{eq}$$

In many cases, particularly for dilute solutions $\gamma(\mathrm{Z})$ is approximately unity but rarely can one ignore the term $\gamma_\pm\left(\mathrm{M^+X^-}\right)$.

$$\text{By definition, } \mathrm{K}^0(\mathrm{app}) = \left\{\mathrm{m(Z)\,m^0}/\left[\mathrm{m}\left(\mathrm{M^+X^-}\right)\right]^2\right\}^{\mathrm{eq}}$$

$$\text{Then, } \ln\mathrm{K}^0(\text{ app }) = \ln\mathrm{K}^0 + 2\ln\left[\gamma_\pm\left(\mathrm{M^+X^-}\right)\right]$$

The solution may be so dilute that the mean ionic activity coefficient can be calculated using the Debye-Huckel Limiting Law (DHLL).

$$\text{Hence} \quad \ln\mathrm{K}^0(\mathrm{app}) = \ln\mathrm{K}^0 - 2\,\mathrm{S}_\gamma\,\left[\mathrm{m}\left(\mathrm{M^+X^-}\right)/\mathrm{m^0}\right]11/2$$

In this equation the negative sign signals that in real solutions the extent of ion association to form $\mathrm{Z(aq)}$ is less than in the corresponding ideal solution because charge - charge interactions in real solutions stabilise the ions.

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1.4.5: Chemical Equilibria- Solutions- Sparingly Soluble Salt

A given aqueous solution contains a sparingly soluble 1:1 salt [e.g. $AgCl(s)$] at fixed temperature and pressure. The following phase equilibrium is established.

$$M^+X^-(s) \rightleftharpoons M^+(aq) + X^-(aq) \tag{1.4.5.1}$$

In terms of the Phase Rule, the system contains two components, water and sparingly soluble substance MX; $C = 2$. There are three phases: solution, vapour and solid. Then $F = 1$. Hence if we define the temperature, the vapour pressure and the equilibrium composition of the liquid phase are defined.

A thermodynamic description of equilibrium (Equation 1.4.5.1) is based on equality of chemical potentials of reactants and products. The key point is that the solid, $M^+X^-(s)$ is a reference state.

$$\text{Hence, } \mu^0\left(M^+X^-;s\right) = \mu^{eq}\left(M^+X^-;aq\right)$$

Noting that M^+X^- is a 1:1 salt,

$$\mu^0(MX;s) = \\ \mu^0\left(M^+X^-;aq\right) + 2\,R\,T\,\ln\left(m\left(M^+X^-\right)\,\gamma_\pm\left(M^+X^-\right)/m^0\right)^{eq}$$

The solubility product for salt M^+X^-, K_s^0 is defined as follows. [K_s^0 is dimensionless.]

$$\Delta_s G^0 = \mu^0\left(M^+X^-;aq\right) - \mu^0\left(M^+X^-;s\right) = -R\,T\,\ln\left(K_s^0\right)$$

$$\text{Hence } [1], K_s^0 = \left[Sol\left(M^+X^-\right)^{eq}\,\gamma_\pm^{eq}\left(M^+X^-\right)/m^0\right]^2$$

$Sol\left(M^+X^-\right)^{eq}$ is the (equilibrium) solubility, a quantity obtained experimentally.

$$\ln\left[Sol\left(M^+X^-\right)^{eq}/m^0\right] = -\ln\left(\gamma_\pm^{eq}\left(M^+X^-\right)\right) + (1/2)\,\ln\left(K_s^0\right)$$

In many cases salt $M^+X^-(s))$ is so sparingly soluble that $\ln\left(\gamma_\pm^{eq}\left(M^+X^-\right)\right)$ can be calculated using the Debye-Huckel Limiting Law (DHLL). The DHLL relates $\ln\left(\gamma_\pm\left(M^+X^-\right)\right)^{eq}$ to the ionic strength of the solution, I. The ionic strength is controlled by adding a second soluble salt N^+Y^-.

$$\ln\left[Sol\left(M^+X^-\right)^{eq}/m^0\right] = S_\gamma\,\left(I/m^0\right)^{1/2} + (1/2)\,\ln\left(K_s^0\right)$$

This is a classic equation [2] because in many cases $\ln\left[Sol\left(M^+X^-\right)^{eq}/m^0\right]$ is a linear function of $\left(I/m^0\right)^{1/2}$ so that $\ln\left(K_S^0\right)$ is obtained from the corresponding intercept. We understand the form of equation (g) in terms of increasing stabilisation of the ions $M^+(aq)$ and $X^-(aq)$ in solution by the ion-ion interactions in the real solution which are enhanced when the ionic strength is increased by adding soluble salt N^+Y^-.

Footnotes

[1] K_s^0 is dimensionless. However in many reports a quantity K_m^0 is defined as follows.

$$K_m^0 = \left[Sol\left(M^+X^-\right)^{eq}\,\gamma_\pm^{eq}\right]^2$$

For a 1:1 salt, K_m^0 has units, $\left(molkg^{-1}\right)^2$. Or $K_s^0 = K_m^0/\left(m^0\right)^2$

[2] All three terms in equation (g) are dimensionless.

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1.4.6: Chemical Equilibria- Cratic and Unitary Quantities

We comment on the term 'equilibrium constant' where the composition of the solution under examination is expressed in terms of solute molalities, solute concentrations and solute mole fractions. [1-5] We consider a closed system in which the solvent is water(λ) at defined temperature and pressure where the pressure is ambient and close to the standard pressure p^0. The solution contains n_1 moles of water and $n_j{}^{\mathrm{eq}}$ moles of each chemical substance j, solutes, where j the composition is described in terms of a chemical equilibrium. The latter is described in the following general terms where ν_j is the stoichiometry for chemical substance j, being positive for products and negative for reactants.

$$\sum_{j=1}^{j=i} v_j \, \mu_j^{eq}(aq) = 0$$

The sum is taken over all i-solutes in solution with respect to the equilibrium chemical potentials of each chemical substance j.

Molalities

The equilibrium molality of solute j is given by the ratio $(\mathrm{n_j}/\mathrm{n_1\,M_1})$ where $\mathrm{M_1}$ is the molar mass of water. From equation (a),

$$\sum_{j=1}^{j=i} v_j \, \left[\mu_j^0(aq;T) + RT \, \ln\left(m_j^{\mathrm{eq}} \gamma_j^{eq}/m^0\right)\right] = 0$$

By definition for each solute j,

$$\mathrm{limit}\,(\mathrm{m_j} \rightarrow 0)\,\gamma_\mathrm{j} = 1.0 \text{ at all T and p}$$

A standard equilibrium constant $\mathrm{K_m}^0$ is defined using equation (d) where the m subscript 'm' is a reminder that we are using molalities to express the composition of the solution under examination.

$$\Delta_\mathrm{r}\mathrm{G}^0(\ \mathrm{T};\mathrm{m}-\ \text{scale}\ ) = -\mathrm{R\,T\,ln}\left[\mathrm{K_m^0}(\ \mathrm{T})\right] = \sum_{\mathrm{j=1}}^{\mathrm{ji}} \mathrm{v_j}\,\mu_\mathrm{j}^0(\mathrm{aq};\mathrm{T})$$

At temperature T, $\mathrm{K_m^0}(\ \mathrm{T})$ is related to the equilibrium composition of the solution using equation (e).

$$\mathrm{K_m^0}(\ \mathrm{T}) = \prod_{\mathrm{j=1}}^{\mathrm{ji}} \left(\mathrm{m_j^{eq}}\,\gamma_\mathrm{j}^{\mathrm{eq}}/\mathrm{m}^0\right)^{v(\mathrm{j})}$$

$$\text{Also by definition, } \mathrm{pK_m^0}(\ \mathrm{T}) = -\lg\left[\mathrm{K_m^0}(\ \mathrm{T})\right]$$

From the Gibbs –Helmholtz Equation ,

$$\Delta_\mathrm{r}\mathrm{H_m^0} = -\mathrm{T}^2\left[\frac{\partial}{\partial \mathrm{T}}\left(\frac{\Delta_\mathrm{r}\mathrm{G_m^0}}{\mathrm{T}}\right)\right]_\mathrm{p} = \mathrm{R\,T}^2\left[\frac{\partial \ln\left(\mathrm{K_m^0}\right)}{\partial \mathrm{T}}\right]_\mathrm{p} = -\mathrm{R}\left[\frac{\partial \ln\left(\mathrm{K_m^0}\right)}{\partial \mathrm{T}^{-1}}\right]_\mathrm{p}$$

$$\Delta_\mathrm{r}\mathrm{C_{pm}^0}(\ \mathrm{T}) = \left[\partial\Delta_\mathrm{r}\mathrm{H_m^0}/\partial\mathrm{T}\right]_\mathrm{p}$$

$$\Delta_\mathrm{r}\mathrm{S_m^0} = \mathrm{T}^{-1}\ \left[\Delta_\mathrm{r}\mathrm{H_m^0} - \Delta_\mathrm{r}\mathrm{G_m^0}\right]$$

The algebra is a little tortuous but the points are clearly made if we confine attention to chemical equilibria in solutions having thermodynamic properties which are ideal. For a chemical equilibrium involving j chemical substances in solution where the solvent is chemical substance 1, at fixed temperature and pressure,

$$\mathrm{K^0} = \prod_{\mathrm{j=2}}^{\mathrm{j=i}} \left(\mathrm{m_j^{eq}}/\mathrm{m}^0\right)^{\mathrm{v_i}}$$

$$\text{Also}\quad \mathrm{K_m^0} = \prod_{\mathrm{j=2}}^{\mathrm{j=i}} \left(\mathrm{m_j^{eq}}\right)^{v_j}$$

$$\Delta_\mathrm{r}\mathrm{G}^0 = -\mathrm{R\,T\,ln\,K}^0$$

$$\Delta_r G^0 = -R\,T\,\ln\left[\prod_{j=2}^{j=i}\left(\frac{m_j^{eq}}{m^0}\right)^{v_j}\right]$$

$$\Delta_r G^0 = -R\,T\,\ln\left[\prod_{j=2}^{j=i}\left(m_j^{eq}\right)^{v_j}\right] + v\,R\,T\,\ln\left(m^0\right)$$

$$\Delta_r G^0 = -R\,T\,\ln K_m^0 + v\,R\,T\,\ln\left(m^0\right)$$

$$\Delta_r G^0 = \Delta_r G_m^0 + V\,R\,T\,\ln\left(m^0\right)$$

$$\Delta_r G_m^0 = -R\,T\,\ln K_m^0$$

This rather dull analysis has merit in showing that the lost units in the equation $\Delta_r G^0 = -R\ T\ \ln K_m^0$ are found in the term $[V\,R\,T\,\ln(m^0)]$ where $V = \sum_{j=2}^{j=i} v_j$. This concern arises because for correct dimensions the logarithm operation should operate on a pure number. No such problems emerge if ν is zero as is the case for a stoichiometrically balanced equilibrium. Moreover if we probe the dependence of K^0 or ${K_m}^0$ on temperature we have that,

$$\frac{d}{dT}\left[\frac{v\,R\,T\,\ln\left(m^0\right)}{T}\right] = 0$$

If we are interested in the dependence of either K^0 or ${K_m}^0$ on pressure, we have that,

$$\frac{d}{dp}\left[v\,R\,T\,\ln\left(m^0\right)\right] = 0$$

Mole Fraction Scale

The total amount of all chemical substances in the closed system, an aqueous solution, at chemical equilibrium is given by equation (t).

$$n_T^{eq} = n_1 + \sum n_j^{eq}$$

For a given chemical substance, solute k

$$x_k^{eq} = n_k^{eq} / \left[n_1 + \sum n_j^{eq}\right]$$

In terms of mole fractions, the equilibrium chemical potential for solute j, $\mu_j^{eq}(aq;T;p)$ is related to the equilibrium mole fraction) $x_j^{eq}(aq)$ using equation (v).

$$\mu_j^{eq}(aq;T;p) = \mu_j^0(x-scale;aq;T) + R\,T\,\ln\left(x_j^{eq}\,f_j^{*eq}\right)$$

$$\text{By definition, at all T and p, } \lim\left(x_j \to 0\right) f_j^* = 1.0.$$

Further,

$$\mu_j^0(x-\ scale;\ aq;\ T)$$

is the chemical potential of substance j in aqueous solution at temperature T in a solution where the mole fraction of solute j is unity. Here therefore $\mu_j^0(x-\ scale;\ aq;\ T)$ is the reference chemical potential. From equation (a),

$$\sum_{j=1}^{j=i} v_j\ \left[\mu_j^0(x-\ scale;\ aq;\ T) + R\,T\,\ln\left(x_j^{eq}\,f_j^{*eq}\right)\right] = 0$$

$$\Delta_r G_x^0(\ T) = -R\,T\,\ln\left[K_x^0(\ T)\right] = \sum_{j=1}^{j=i} v_j\,\mu_j^0(x-\ scale;\ aq;\ T)$$

(T) R T ln[K (T)] (x scale;aq;T) At temperature T, $K_x^0(\ T)$ is related to the equilibrium mole fractions of the solutes.

$$K_x^0(\ T) = \prod_{j=1}^{j=i}\left(x_j^{eq}\,f_j^{*eq}\right)^{v(j)}$$

From the Gibbs –Helmholtz Equation,

$$\Delta_r H_x^0 = -T^2 \left[\frac{\partial}{\partial T}\left(\frac{\Delta_r G_x^0}{T}\right)\right]_p = R\,T^2 \left[\frac{\partial \ln\left(K_x^0\right)}{\partial T}\right]_p = -R \left[\frac{\partial \ln\left(K_x^0\right)}{\partial T^{-1}}\right]_p$$

$$\Delta_r C_{px}^0(\ T) = \left[\partial \Delta_r H_x^0 / \partial T\right]_p$$

$$\Delta_r S_x^0 = T^{-1}\ \left[\Delta_r H_x^0 - \Delta_r G_x^0\right]$$

We note a complication. We suppose that the composition of a given closed system, an aqueous solution, is described in terms of the formation of a dimer by a solute Z in aqueous solution at defined T and p

$$2Z(aq) \Longleftrightarrow Z_2(aq)$$

At equilibrium, the solution contains n1 moles of water, $n^{eq}(Z)$ moles of monomer and $n^{eq}\left(Z_2\right)$ moles of dimer.

$$x(Z)^{eq} = n(Z)^{eq} / \left[n_1 + n(Z)^{eq} + n\left(Z_2\right)^{eq}\right]$$

$$x\left(Z_2\right)^{eq}\ = n\left(Z_2\right)^{eq}\ / \left[n_1 + n(Z)^{eq} + n\left(Z_2\right)^{eq}\right]$$

$$\text{Further, } x_1^{eq} = n_1 / \left[n_1 + n(Z)^{eq} + n\left(Z_2\right)^{eq}\right]$$

As a result of a change in temperature $n^{eq}(Z)$ and $n^{eq}\left(Z_2\right)$ change; n_1 does not. For example $x(Z)^{eq}$ changes as a result of changes in both numerator and denominator in equation (ze). This unwelcome complication is not encountered if we use the molality scale. The way forward is to confine attention to dilute solutions such that at all temperatures, $\sum_{j=2}^{j=i} n_j^{eq} << n_1$.

Mole Fraction and Molality Scales

The complication noted in conjunction with equation (zd) also emerges when equilibrium constants on these two scales are compared. If the thermodynamic properties of the solutions are ideal, we obtain the following two equations.

$$K_m^0(\ T) = \prod_{j=1}^{j=i} \left(m_j^{eq} / m^0\right)^{v(j)}$$

$$K_x^0(\ T) = \prod_{j=1}^{j=i} \left(x_j^{eq}\right)^{v(j)}$$

$$K_m^0(\ T) / K_x^0(\ T) = \prod_{j=1}^{j=i} \left(m_j^{eq} / m^0\, x_j^{eq}\right)^{v(j)}$$

But $m_j^{eq} = n_j^{eq} / w_1 = n_j^{eq} / n_1\, M_1$

For dilute solutions $x_j^{eq} = n_j^{eq} / n_1\ \frac{m_j}{m^0\, x_j^{eq}} = \frac{n_j^{eq}}{n_1\, M_1\, m^0}\ \frac{n_1}{n_j^{eq}}$

$$\prod_{j=1}^{j=i} \left[\frac{n_j^{eq}}{n_1\, M_1\, m^0}\ \frac{n_1}{n_j^{eq}}\right]^{v(j)} = \prod_{j=1}^{j=1} \left[\frac{1}{M_1\, m^0}\right]^{v(j)}$$

The product $\left(M_1\, m^0\right)$ is dimensionless; i.e. $\left(kgmol^{-1}\right)\ \left(molkg^{-1}\right)$.

$$\text{Hence, } K_x^0(\ T) = K_m^0(\ T) \prod_{j=1}^{j=i} \left(M_1\, m^0\right)^{v(j)}$$

Consider a chemical equilibrium which has the following form,

$$A(aq) \Leftrightarrow = B(aq)$$

$$K_x^0(\ T) = K_m^0(\ T)\ \left(M_1\, m^0\right)^{+1}\ \left(M_1\, m^0\right)^{-1}$$

$$K_x^0(\ T) = K_m^0(\ T)$$

In fact for all symmetric equilibria in dilute solution, the numerical values of $K_x^0(\ T)$ and $K_m^0(\ T)$ are equal.

Concentration Scale

The main advantage from a thermodynamic standpoint in expressing the composition of a solution in terms of molalities, m_j is the fact that the definition does not require specification of either temperature or pressure. The latter is a consequence of using a definition based on the masses of solvent and solute. Nevertheless from a practical standpoint there are many advantages in expressing the composition of a solution in terms of concentration $\mathrm{c_j} (= \mathrm{n_j/V}$ where V is the volume of a solution). Many experimental techniques are based on 'counting' the amount of solute j in a given volume of system. This is certainly true of uv/visible spectrophotometric methods based on Beer's Law. Similarly electrical conductivities count the amount of conducting ions in a given volume of solution. Further when these methods are used, the actual densities of the solutions are only rarely measured so that conversion from concentration c_j to molality m_j is not straightforward.

We may find it convenient to characterise the composition of a given aqueous solution in terms of equilibrium concentrations of each solute j. Therefore the volume of the aqueous solution $\mathrm{V^{eq}(aq;T;p)}$ is given by equation (zp).

$$\mathrm{V^{eq}(aq;T;p) = n_1\, V_1^{eq}(aq;T;p;) + \sum_{j=2}^{j=i} n_j^{eq}\, V_j^{eq}(aq;T;p)}$$

$$\mathrm{For\ solute\ j, c_j^{eq} = n_j^{eq}/V^{eq}(aq;T;p)}$$

At this point a problem emerges. Even in the event that $\mathbf{n}_\mathrm{j}^{\mathrm{eq}}$ does not change when the temperature is changed, $\mathbf{c}_\mathrm{j}^{\mathrm{eq}}$ changes because for real solutions $\mathrm{V}^{eq}(\mathrm{aq;T;p})$ is dependent on temperature. Furthermore at fixed T, p and composition, the volume of the corresponding ideal solution differs from $\mathrm{V^{eq}(aq;T;p)}$ and hence $\mathrm{c_j^{id} \neq c_j^{eq}}$. The way forward explores chemical equilibria in very dilute solutions.

$$\mathrm{\sum_{j=2}^{j=i} n_j^{eq}\, V_j^{eq}(aq;T;p) \ll n_1\, V_1^{eq}(aq;T;p;)}$$

$$\mathrm{Hence,}\quad V^{\mathrm{eq}}\,(\mathrm{aq};T;p) = \mathrm{n_1\, V_1^*(\lambda;T;p)}$$

$$\mathrm{Therefore,\ c_j^{eq} = n_j^{eq}/n_1\, V_1^*(\lambda)}$$

We express the chemical potential $\mu_j^{eq}(\mathrm{aq})$ using equation (zu).

$$\mathrm{\mu_j^{eq}(aq;T;p) = \mu_j^0(c-\ scale;\ aq;T) + R\,T\,\ln\left(c_j^{eq}\, y_j^{eq}/c_r\right)}$$

Here $\mathrm{c_r = 1\ moldm^{-3}}$, $\mathrm{c_j^{eq}}$ being expressed using the unit, $\mathrm{mol\ dm^{-3}}$; $\mathrm{y_j^{eq}}$ is the activity coefficient for solute j on the concentration scale, describing the impact of solute-solute interactions in the aqueous solution. By definition at all T and p,

$$\mathrm{limit}\,(c_j \to 0)\, y_j = 1.0$$

From equation (a),

$$\sum_{j=1}^{j=i} v_j\ \left[\mu_j^0(c-scale;aq;T) + RT\,\ln\left(c_j^{eq}\, y_j^{eq}/c_r\right)\right] = 0$$

By definition,

$$\mathrm{\Delta_r G_c^0(\ T) = -R\,T\,\ln\left[K_c(T)\right] = \sum_{j=1}^{j=i} v_j\, \mu_j^0(c-\ scale;\ aq;\ T)}$$

$$K_c(T) = \prod_{j=1}^{j=i}\left(c_j^{eq}\, y_j^{eq}/c_f\right)^{v(j)}$$

For dilute solutions we might assume that $\mathrm{y_j^{eq}}$ is unity for all solutes.

$$K_c(T) = \prod_{j=1}^{j=1}\left(c_j^{eq}/c_r\right)^{v(j)}$$

From the Gibbs - Helmholtz Equation,

$$\Delta_r H_c^0 = -T^2 \left[\frac{\partial}{\partial T}\left(\frac{\Delta_r G_c^0}{T}\right)\right]_p = R\,T^2 \left[\frac{\partial \ln(K_c)}{\partial T}\right]_p = -R \left[\frac{\partial \ln(K_c)}{\partial T^{-1}}\right]_p$$

$$\Delta_r C_{pc}^0(T) = \left[\partial \Delta_r H_c^0 / \partial T\right]_p$$

$$\Delta_r S_c^0 = T^{-1}\left[\Delta_r H_c^0 - \Delta_r G_c^0\right]$$

Molality and Concentration Scales

If the thermodynamic properties of the solutions are ideal, we obtain the following two equations.

$$K_m^0(T) = \prod_{j=1}^{ji} \left(m_j^{eq}/m^0\right)^{v(j)}$$

$$K_c^0(T) = \prod_{j=1}^{j=i} \left(c_j^{eq}/c_r\right)^{v(j)}$$

$$K_m^0(T)/K_c^0(T) = \prod_{j=1}^{j=i} \left(m_j^{eq}\, c_r / c_j^{eq}\, m^0\right)^{v(j)}$$

But $m_j^{eq} = n_j^{eq}/w_1 = n_j^{eq}/n_1\, M_1$

$$\text{And for dilute solutions, } c_j^{eq} = n_j^{eq}/V(aq) = n_j^{eq}/n_1\, V_1^*$$

$$m_j^{eq}/c_j^{eq} = V_1^*(\lambda)/M_1 = 1/\rho_1^*(\lambda)$$

By definition, $\rho^0 = c_r/m^0 = \left[\text{moldm}^{-3}\right] / \left[\text{molkg}^{-1}\right] = \left[\text{kgdm}^{-3}\right]$

By introducing the property ρ^0 we overcome the problem with units.

$$K_m^0(T)/K_c^0(T) = \prod_{j=1}^{j=i} \left(\rho_1^*(\lambda)/\rho^0\right)^{v(j)}$$

A scale factor of 10^3 often occurs in these equations because concentrations are conventionally quoted using the unit, moldm^{-3} and densities are expressed using the unit, gcm^{-3}.

In summary care should be taken when using equilibrium constants based on different composition scales. [1-4] A classic example [5] from the field of kinetics shows how misleading conclusions can be drawn from, for example, comparison of standard entropies of activation and reaction expressed using different composition scales. [6]

Footnotes

[1] L. Hepler, Thermochim Acta,1981,**50**,69.

[2] E. A. Guggenheim, Trans. Faraday Soc.,1937,**33**,607.

[3] E. Euranto, J.J.Kankare and N.J.Cleve, J. Chem. Eng. Data,1969, **14**, 455.

[4] R. W. Gurney, Ionic Processes in Solution , McGraw-Hill, New York, 1952.

[5] As Guggenheim remarked the units of $\ln(V)$ are $\ln(m^3)$. If $V = 100\ m^3$, then $\log(V) = \log(100) + \log(m^3)$, $\log(V) - \log(m^3) = 2$; $\log(V/m^3) = 2$.

[6] M. H. Abraham and A. Nasehzadeh, J. Chem. Soc. Chem. Commun., 1981, 905.

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1.4.7: Chemical Equilibria- Composition- Temperature and Pressure Dependence

The variable ξ describes in quite general terms molecular composition – molecular organisation. For a given closed system at fixed T and p there exists a composition-organisation \(\xi_{\mathrm{eq}}\) corresponding to a minimum in Gibbs energy where the affinity for spontaneous change is zero. In general terms there exists an extent of reaction ξ corresponding to a given affinity A at defined T and p. In fact we can express ξ as a dependent variable defined by the independent variables, T, p and A.

$$\xi = \xi[T, p, A]$$

The general differential of equation (a) takes the following form.

$$\mathrm{d}\xi = \left(\frac{\partial \xi}{\partial T}\right)_{\mathrm{p,A}} \mathrm{dT} + \left(\frac{\partial \xi}{\partial \mathrm{p}}\right)_{\mathrm{T,A}} \mathrm{dp} + \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}} \mathrm{dA}$$

Equation (b) describes the dependence of extent of reaction on changes in T, p and affinity A.

$$\text{Moreover, } \left(\frac{\partial \xi}{\partial T}\right)_{\mathrm{p,A}} = -\left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}} \left[\frac{1}{\mathrm{T}} \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}} + \frac{\mathrm{A}}{\mathrm{T}}\right]$$

At equilibrium where '$\mathrm{A} = 0$' and $(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}} < 0$, then

$$\left(\frac{\partial \xi}{\partial T}\right)_{p,A=0} \text{ takes the sign of } \left[\frac{1}{T} \left(\frac{\partial H}{\partial \xi}\right)_{T,p}^{eq}\right] = \left[\frac{1}{T} \sum_{j=1}^{j=i} v_j H_j^{eq}\right]$$

$$\text{Similarly, } \left(\frac{\partial \xi}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} \text{ takes the sign of } \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}} \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}}$$

Again at equilibrium where '$\mathrm{A} = 0$' and $(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}} < 0$, then

$$\left(\frac{\partial \xi}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} \text{ takes the sign of } \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}}^{\mathrm{eq}} = -\sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{v_j\, V_j^{eq}}$$

Equations (d) and (f) are important being universally valid and forming the basis of important generalisations, the Laws of Moderation.

Equation (d) shows that the differential dependence of composition on temperature is related to the enthalpy of reaction. If the chemical reaction is exothermic {i.e. $\left(\frac{\partial H}{\partial \xi}\right)_{\mathrm{T,p}}^{\mathrm{eq}}$ is negative}, the chemical equilibrium shifts to favour an increase in the amount of reactants. Whereas if the reaction is endothermic , the composition swings in a direction to favour the products.

In another experiment, the equilibrium system is perturbed by an increase in pressure. Equation (f) shows that the equilibrium composition swings to favour the reactants if the volume of reaction is positive. Alternatively if the volume of reaction is negative, the composition of the system changes to favour products [1].

Footnotes

[1] The conclusions reached here are called 'Theorems of Moderation'. MJB was taught that the outcome is 'Nature's Laws of Cussedness' [= obstinacy]. An exothermic reaction generates heat to raise the temperature of the system, so the system responds, when the temperature is raised, by shifting the equilibrium in the direction for which the process is endothermic. The line of argument is not good thermodynamics but it makes the point.

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1.4.8: Chemical Equilibrium Constants- Dependence on Temperature at Fixed Pressure

A given set of data reports the dependence on temperature (at fixed pressure p, which is close to the standard pressure p^0) of K^0 for a given chemical equilibrium.[1 - 3]

$$\Delta_{\mathrm{r}}\mathrm{G}^0 = -\mathrm{RT}\ln \mathrm{K}^0 = \Delta\mathrm{H}^0 - \mathrm{T}\Delta_{\mathrm{r}}\mathrm{S}^0$$

If we confine our attention to systems where the chemical equilibria involve solutes in dilute solution in a given solvent, we can replace $\Delta_{\mathrm{r}}\mathrm{H}^0$ in this equation with the limiting enthalpy of reaction, $\Delta_{\mathrm{r}}\mathrm{H}^\infty$. According to the Gibbs - Helmholtz Equation, at fixed pressure,

$$\frac{\mathrm{d}\left[\Delta_{\mathrm{r}}\mathrm{G}^0/\mathrm{T}\right]}{\mathrm{dT}} = -\frac{\Delta_{\mathrm{r}}\mathrm{H}^\infty}{\mathrm{T}^2}$$

Hence

$$\frac{\mathrm{d}\ln\left(\mathrm{K}^0\right)}{\mathrm{dT}} = \frac{\Delta_{\mathrm{r}}\mathrm{H}^\infty}{\mathrm{RT}^2}$$

or, [4]

$$\frac{\mathrm{d}\ln \mathrm{K}^0}{\mathrm{dT}^{-1}} = -\frac{\Delta_{\mathrm{r}}\mathrm{H}^\infty}{\mathrm{R}}$$

The latter two equations are equivalent forms of the van 't Hoff Equation expressing the dependence of K^0 on temperature. This equation does not predict how equilibrium constants depend on temperature. For example the van't Hoff equation does not require that $\ln\left(\mathrm{K}^0\right)$ is a linear function of $\mathrm{T}-1$. In fact for simple carboxylic acids, the plots of $\ln(\text{acid dissociation constant})$ against temperature show maxima. For example, $\ln\left(\mathrm{K}^0\right)$ for the acid dissociation constant of ethanoic acid in aqueous solution at ambient pressure increases with increase in temperature, passes through a maximum near $295\ \mathrm{K}$ and then decreases. [5-7] At the temperature where K^0 is a maximum, the limiting enthalpy of dissociation is zero. This pattern is possibly surprising at first sight but can be understood in terms of a balance between the standard enthalpy of heterolytic fission of the $\mathrm{O}-\mathrm{H}$ group in the carboxylic acid group and the standard enthalpies of hydration of the resulting hydrogen and carboxylate ions.

Thus the dependence of K^0 on temperature can be obtained experimentally, the dependence being unique for each system [8]. Nevertheless these equations signal how the dependence forms the basis for determining limiting enthalpies of reaction. The analysis also recognises that $\Delta_{\mathrm{r}}\mathrm{H}^0$ is likely to depend on temperature. There is merit in expressing the dependence of K^0 on temperature about a reference temperature θ, chosen near the middle of the experimental temperature range [2,3,9]. Over the experimental temperature range straddling θ, we express the dependence of K^0 on temperature using the integrated form of equation (c).

$$\ln\left[\mathrm{K}^0(\ \mathrm{T})\right] = \ln\left[\mathrm{K}^0(\theta)\right] + \int_\theta^{\mathrm{T}}\left[\frac{\Delta_{\mathrm{r}}\mathrm{H}^\omega}{\mathrm{RT}^2}\right]\mathrm{dT}$$

By definition, the limiting isobaric heat capacity of reaction $\Delta_{\mathrm{r}}C_{\mathrm{p}}^\infty$ is given by equation (f).

$$\Delta_{\mathrm{r}}\mathrm{C}_{\mathrm{p}}^\infty = \left(\frac{\mathrm{d}\Delta_{\mathrm{r}}\mathrm{H}^\infty}{\mathrm{dT}}\right)_{\mathrm{p}}$$

The analysis becomes complicated because we recognise that $\Delta_{\mathrm{r}}C_{\mathrm{p}}^\infty$ depends on temperature. [9] In fact only in rare instances are experimental results sufficiently precise to warrant taking such a dependence into account. [10] A reasonable assumption is that $\Delta_r C_p^\infty$ is independent of temperature such that $\Delta_{\mathrm{r}}\mathrm{H}^\infty$ is a linear function of temperature over the experimental temperature range. [11]

$$\Delta_{\mathrm{r}}\mathrm{H}^\infty(\mathrm{T}) = \Delta_{\mathrm{r}}\mathrm{H}^\infty(\theta) + \Delta_{\mathrm{r}}\mathrm{C}_{\mathrm{p}}^\infty(\mathrm{T}-\theta)$$

Hence,

$$\ln\left[\mathrm{K}^0(\ \mathrm{T})\right] =$$
$$\ln\left[\mathrm{K}^0(\theta)\right] + \frac{1}{\mathrm{R}}\int_\theta^{\mathrm{T}}\left[\frac{\Delta_\mathrm{r}\mathrm{H}^\infty(\theta)}{\mathrm{T}^2} + \Delta_\mathrm{r}\mathrm{C}_\mathrm{p}^\infty\left(\frac{1}{\mathrm{T}} - \frac{\theta}{\mathrm{T}^2}\right)\right]\mathrm{dT}$$

Hence,

$$\ln\left[\mathrm{K}^0(\ \mathrm{T})\right] =$$
$$\ln\left[\mathrm{K}^0(\theta)\right] + \frac{\Delta_\mathrm{r}\mathrm{H}^\infty(\theta)}{\mathrm{R}}\left[\frac{1}{\theta} - \frac{1}{\mathrm{T}}\right] + \frac{\Delta_\mathrm{r}\mathrm{C}_\mathrm{p}^\infty}{\mathrm{R}}\left[\frac{\theta}{\mathrm{T}} - 1 + \ln\left(\frac{\mathrm{T}}{\theta}\right)\right]$$

Numerical analysis uses linear least squares procedures with reference to the dependence of $\ln K^0(T)$ on temperature about the reference temperature θ in order to obtain estimates of $\Delta_\mathrm{r}\mathrm{H}^\infty(\theta)$ and $\Delta_r C_p^\infty$. The coupling of estimates of derived parameters is minimal if θ is chosen near the centre of the measured temperature range. [2,3] Granted that the analysis yields $\Delta_\mathrm{r}\mathrm{H}^\infty$ at a given temperature and pressure, combination with the corresponding $\Delta_\mathrm{r}\mathrm{G}^0$ yields the entropy term, $\Delta_\mathrm{r}\mathrm{S}^0$.

Other methods of data analysis in this context use (a) orthogonal polynomials, [12] and (b) sigma plots. [13]

An extensive literature describes the thermodynamics of acid dissociation in alcohol + water mixtures. In these solvent systems the standard enthalpies and other thermodynamic parameters pass through extrema as the mole fraction composition of the solvent is changed. [14- 18]

Perlmutter-Hayman examines the related problem of the dependence on temperature of activation energies [19].

Enthalpies of dissociation for weak acids in aqueous solution can be obtained calorimetrically. [20]

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1.4.9: Chemical Equilibria- Dependence on Pressure at Fixed Temperature

A key quantity in the description of a chemical equilibrium is the equilibrium constant. In the majority of cases the symbol used is K^0 indicating with the superscript '0' a standard property. This symbol is used because, again in the majority of cases an equilibrium constant refers to a system at ambient pressure which is close to the standard pressure; i.e. 10^5 Pa. In reporting K^0 therefore the temperature is stated but by definition K^0 is not dependent on pressure. However the equilibrium composition of a closed system generally depends on pressure at fixed temperature T. This problem over symbols and nomenclature is resolved as follows [1-7].

An aqueous solution contains i-chemical substances, solutes, in chemical equilibrium. For a given solute–j the dependence of chemical potential $\mu_j(aq;T;p)$ on molality m_j is given by equation (a).

$$\mu_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^0\right) + \int_{\mathrm{p}^\circ}^{\mathrm{p}} \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq})\,\mathrm{dp}$$

We define a reference chemical potential for solute-j μ_j^* at temperature T and pressure p using equation (b).

$$\mu_{\mathrm{j}}^{\#}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T}) + \int_{\mathrm{p}^0}^{\mathrm{p}} \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq})\,\mathrm{dp}$$

Combination of equations (a) and (b) yields equation (c).

$$\mu_j(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{\#}(\mathrm{aq};\mathrm{T};\mathrm{p}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^0\right)$$

XK

Here $\mu_j^H(\mathrm{aq};\mathrm{T};\mathrm{p})$ is the chemical potential of solute-j in an ideal solution (i.e. $\gamma_j = 1$) having unit molality (i.e. $\mathrm{m_j} = 1\ \mathrm{mol\ kg^{-1}}$) at specified T and p. At equilibrium at pressure p and temperature T,

$$\sum_{j=1}^{j=i} v_j\,\mu_j^{\mathrm{eq}}(\mathrm{aq};T;p) = 0$$

By definition,

$$\Delta_{\mathrm{r}}\mathrm{G}^*(\mathrm{aq};\mathrm{T};\mathrm{p}) = \sum \mathrm{v_j}\,\mu_{\mathrm{j}}^*(\mathrm{aq};\mathrm{T};\mathrm{p}) = -\mathrm{R\,T\,ln\,K}^*(\mathrm{T},\mathrm{p})$$

$$\text{and } \mathrm{K}^{\#}(\mathrm{T},\mathrm{p}) = \prod_{\mathrm{j}=1}^{\mathrm{j}=1}\left[\left(\mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}/\mathrm{m}^0\right)\gamma_j^{eq}\right]^{v(j)}$$

The differential dependence on pressure [8,9] of $\mathrm{K}^{\#}(\mathrm{T},\mathrm{p})$ yields the limiting volume of reaction, $\Delta_{\mathrm{r}}\mathrm{V}^{\infty}$.

$$\Delta_r V^{\infty} = \sum_{j=1}^{j=i} V_j\,V_j^{\infty}(aq;T;p) = 0$$

$$\text{and [c.f. V} = [\partial \mathrm{G}/\partial \mathrm{p}]_{\mathrm{T}}]\ \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \left[\partial \mu_{\mathrm{j}}^*(\mathrm{aq})/\partial \mathrm{p}\right]_{\mathrm{T}}$$

$$\text{Hence at pressure } p,\ \left(\frac{\partial \Delta_{\mathrm{r}}\mathrm{G}^*(\mathrm{T})}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \Delta_{\mathrm{r}}\mathrm{V}^{\infty}(\mathrm{T},\mathrm{p})$$

$$\text{or, } \left(\frac{\partial \ln \mathrm{K}''(\mathrm{T})}{\partial \mathrm{p}}\right)_{\mathrm{T}} = -\frac{\Delta_{\mathrm{r}}\mathrm{V}^{\infty}(\mathrm{T},\mathrm{p})}{\mathrm{R\,T}}$$

The negative sign in equation (j) means that if $\ln \mathrm{K}^{\#}$ for a given chemical equilibrium increases with increases in pressure then $\Delta_{\mathrm{r}}\mathrm{V}^{\infty}$ is negative. But thermodynamics does not define how a given equilibrium constant depends on pressure. This dependence must be measured. Moreover we cannot assume that the limiting volume of reaction $\Delta_{\mathrm{r}}\mathrm{V}^{\infty}$ is independent of pressure. This dependence is described by the limiting isothermal compressions of reaction, $\Delta_{\mathrm{r}}\mathrm{K}_{\mathrm{T}}^{\infty}$.

$$\Delta_{\mathrm{r}}\mathrm{K}_{\mathrm{T}}^{\infty} = -\left[\frac{\mathrm{d}\Delta_{\mathrm{r}}\mathrm{V}^{\infty}}{\mathrm{dp}}\right]_{\mathrm{T}}$$

Indeed we cannot assume that $\mathrm{K_T^\infty}$ is independent of pressure but in most cases the precision of the data is insufficient to obtain a meaningful estimate of this dependence. Hence we are often justified in assuming that $\Delta_\mathrm{r}\mathrm{V}^\infty$ is a linear function of pressure about a reference pressure π, the latter usually chosen as ambient pressure. [10]

$$\Delta_\mathrm{r}\mathrm{V}^\infty(\mathrm{p}) = \Delta_\mathrm{r}\mathrm{V}^\infty(\pi) - \Delta_\mathrm{r}\mathrm{K_T^\infty}(\mathrm{p}-\pi)$$

Hence, [11]

$$\ln\left(\mathrm{K}^\#(\mathrm{p})\right) = \ln\left(\mathrm{K}^\#(\pi)\right) - (\mathrm{R\,T})^{-1}\,\Delta_\mathrm{r}\mathrm{V}^\infty(\pi)\,(\mathrm{p}-\pi) - (2\,RT)^{-1}\,\Delta_r K_T^\infty\ \left((p-\pi)^2\right)$$

Thus, $\ln \mathrm{K}^\#(\mathrm{p})$ is a quadratic in $(\mathrm{p}-\pi)$.

Alternatively we may express the dependence of $\ln\left[\mathrm{K}^\#(\mathrm{p})/\mathrm{K}^\#(\pi)\right]$ on pressure using the following equation. [12,13]

$$\mathrm{R\,T}\,\ln\left[\mathrm{K}^\#(\mathrm{p})/\mathrm{K}^\#(\pi)\right] = \\ -\Delta_\mathrm{r}\mathrm{V}^\infty(\pi)\,(\mathrm{p}-\pi) - 0.5\,\Delta_\mathrm{r}\mathrm{K_T^\infty}\,(\mathrm{p}-\pi)^2$$

This equation shows how $\left[\mathrm{K}^\#(\mathrm{p})/\mathrm{K}^\#(\pi)\right]$ may be calculated from estimates of $\Delta_\mathrm{r}\mathrm{V}^\infty(\pi)$ obtained from independently obtained estimates of partial molar volumes and partial molar isothermal compressions of the chemical substances involved in the chemical equilibrium; e.g. acid dissociation of boric acid. [14,15]

Another approach expresses the ratio $\left[\mathrm{K}^\#(\mathrm{p})/\mathrm{K}^\#(\pi)\right]$ as a function of solvent density at pressure p, $\rho(p)$ together with density $\rho(\pi)$ at pressure π and a parameter β using equation (o) [16].

$$\ln\left[K^\#(\mathrm{p})/\mathrm{K}^\#(\pi)\right] = (\beta-1)\,\ln[\rho(\pi)/\rho(\mathrm{p})]$$

This approach is closely linked to numerical analysis based on equation (p). [17]

$$\ln\left[K^\#(p)/K^\#(\pi)\right] = -\left[\Delta_r V^\infty(\pi)/RT\right]\,[p/(1+b\,p)]$$

A rather different approach for chemical equilibria between solutes in aqueous solutions refers to equation (q). A and B are constants independent of pressure but dependent on temperature; these constants describe the dependence of the molar volume of water on pressure at fixed temperature; Tait's isotherm [2,18-21].

$$\mathrm{V_1^*(p)} = \mathrm{V_1^*}(\pi)\,\left[1-\mathrm{A}\,\ln\left(\frac{\mathrm{B}+\mathrm{p}}{\mathrm{B}+\pi}\right)\right]$$

There are a few case where the experimental data warrant consideration of the dependence on pressure of $\Delta_r K^\infty$. Under these circumstances the Owen-Brinkley equation has the following form [2].

$$\mathrm{R\,T}\,\ln\left[\frac{\mathrm{K}^\#(\mathrm{p})}{\mathrm{K}^\#(\pi)}\right] = -\Delta_\mathrm{r}\mathrm{V}^\infty(\pi)\,(\mathrm{p}-\pi) \\ + \Delta_\mathrm{r}\mathrm{K_T^\infty}(\pi)\,\left[(\mathrm{B}+\pi)\,(\mathrm{p}-\pi) - (\mathrm{B}+\pi)^2\,\ln\left(\frac{\mathrm{B}+\mathrm{p}}{\mathrm{B}+\pi}\right)\right]$$

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[10] $\Delta_{\mathrm{r}}\mathrm{V}^{\infty}(\mathrm{p}) = \left[\mathrm{m}^{3}\ \mathrm{mol}^{-1}\right] + \left(\frac{\left[\mathrm{m}^{3}\ \mathrm{mol}^{-1}\right]}{\left[\mathrm{Nm}^{-2}\right]}\right)\ \left[\mathrm{Nm}^{-2}\right]$

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1.5.1: Chemical Potentials, Composition and the Gas Constant

In many Topics describing the thermodynamic properties of liquid mixtures and solutions, key equations relate the chemical potentials of components to the composition of a given system. For example in the case of a binary aqueous mixture the chemical potential of water $\mu_1(\mathrm{T,p,mix})$ is related to the mole fraction of water x_1 at temperature T and pressure p using equation (a).

$$\mu_1(\mathrm{T,p,mix}) = \mu_1^*(\mathrm{T,p},\ell) + \mathrm{R\,T\,ln\,(x_1\,f_1)}$$

$$\text{By definition, limit } (\mathrm{x_1} \rightarrow 1)\,\mathrm{f_1} = 1.0$$

Here $\mu_1^*(\mathrm{T,p},\ell)$ is the chemical potential of water(ℓ) at the same T and p; $\mathrm{f_1}$ is the rational activity coefficient of water in the mixture.

Similarly for solute j in an aqueous solution at temperature T and pressure p, the chemical potential of solute j, $\mu_j(T,p,aq)$ is related to the molality mj using equation (c) where $\mathrm{m^0} = 1\ \mathrm{mol\ kg^{-1}}$.

$$\mu_\mathrm{j}(\mathrm{aq,T,p}) = \mu_\mathrm{j}^0(\mathrm{aq,T,p}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m^0}\right)$$

$$\text{By definition, at all T and } p \text{ limit } (\mathrm{m_j} \rightarrow 0)\,\gamma_\mathrm{j} = 1.0$$

Here $\mu_\mathrm{j}^0(\mathrm{aq,T,p})$ is the chemical potentials of solute j in an aqueous solution at the same T and p where $\mathrm{m_j} = 1.0\ \mathrm{mol\ kg}$ and $\gamma_\mathrm{j} = 1.0$.

In equations (a) and (c) the parameter R is the Gas Constant, $8.314\ \mathrm{Jmol^{-1}\ K^{-1}}$. The word 'Gas' in the latter sentence is interesting bearing in mind that equations (a) and (c) describe the properties of liquids, mixtures and solutions. Here we examine how this parameter emerges in these equations.

The starting point is a description of a closed system containing i–chemical substances, the amount of chemical substance j being n_j.

$$\text{Then, } \mathrm{G} = \mathrm{G}\left[\mathrm{T,p,n_i}\right]$$

The chemical potential $\mu_j(T,p)$ of chemical substance j is given by equation (f).

$$\mu_\mathrm{j}(\mathrm{T,p}) = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}}$$

Moreover the partial molar volume V_j of chemical substance j is given by equation (g).

$$V_j = \left(\frac{\partial \mu_j}{\partial p}\right)_T$$

We simplify the argument by considering a system comprising pure chemical substance 1.

$$\text{Then} \quad \mathrm{V_1^*} = \left(\frac{\partial \mu_1^*}{\partial \mathrm{p}}\right)_\mathrm{T}$$

Thus $\mathrm{V_1^*(T,p)}$ is the molar volume of pure substance 1 at temperature T and pressure p. In the event that chemical substance 1 is a perfect (ideal) gas, the following equation describes the $p-\mathrm{V}-\mathrm{T}$ properties.

$$p_1^*\,V_1^*(g) = RT$$

We write equation (h) in the following form describing an ideal gas at constant temperature T.

$$d\mu_1^*(g) = V_1^*(g)\,dp$$

Equations (i) and (j) yield equation (k).

$$\mathrm{d}\mu_1^*(\mathrm{\ g}) = \mathrm{R\,T\,d\,ln\,p_1^*}$$

We integrate equation (k) between limits p_1^* and p^0 where p^0 is the standard pressure, $101325\ \mathrm{Nm^{-2}}$.

$$\text{Hence, at temperature T, } \mu_1^*(\mathrm{\ g;T;p_1^*}) = \mu_1^*(\mathrm{\ g;T;p^0}) + \mathrm{R\,T\,ln}\left(\mathrm{p_1^*/p^0}\right)$$

In a more complicated system, the gas phase is a gaseous mixture, comprising two components, component 1 and component 2 with partial pressures $\mathrm{p_1}$ and $\mathrm{p_2}$. We assume the thermodynamic properties of the gas phase in equilibrium with a liquid phase are ideal. Hence equation (l) takes the following form where $\mu_1\,(g;\ \mathrm{mix};\ p_1)$ is the chemical potential of gas-1 at partial pressure $\mathrm{p_1}$.

$$\mu_1^{\mathrm{eq}}\,(\mathrm{g;mix;id;T;p_1}) = \mu_1^*\,(\ \mathrm{g;T;p^0}) + \mathrm{R\,T\,\ln\left(p_1^{eq}/p^0\right)}$$

Liquid Mixtures

A given closed system contains chemical substances 1 and 2, present in two phases, gas and a liquid mixture at temperature T and pressure p. Thus $\mathrm{p_1^{eq}}$ is the equilibrium partial pressure of chemical substance 1 in the gas phase. At equilibrium the chemical potentials of chemical substance 1 in the vapour and liquid mixture phases are equal.

$$\mu_1^{\mathrm{eq}}(\ell;\mathrm{mix;id;p;T}) = \mu_1^{\mathrm{eq}}\,(\mathrm{g;mix;T;p_1^{eq}})$$

Thus $\mathrm{p_1^{eq}}$ is the partial pressure of chemical substance 1 in the gas phase, the superscript 'eq' indicating an equilibrium with the liquid phase at pressure p; the complete system is at temperature T.

Hence using equations (m) and (n) we obtain an equation for the equilibrium chemical potential of chemical substance 1 in an ideal liquid mixture at temperature T and pressure p

$$\mu_1^{\mathrm{eq}}\,(\ell;\mathrm{mix;id;p;T}) = \mu_1^*\,(\ \mathrm{g;p^0;T}) + \mathrm{R\,T\,\ln\left(p_1^{eq}/p^0\right)}$$

The thermodynamic analysis calls on the results of experiments in which the partial pressure p_i of chemical substance-i in a liquid mixture at temperature T is measured as a function of mole fraction x_i. It turns out that for nearly all liquid mixtures at fixed temperature, p_i is approximately a linear function of the mole fraction $\mathrm{x_1}$ at low $\mathrm{x_1}$. We therefore define an ideal liquid mixture. By definition the (equilibrium) vapour pressure of chemical substance i, one component of a liquid mixture, is related to the mole fraction composition at temperature T using equation (p).

$$\mathrm{Thus\ p_i^{eq}(T;\ mix\ ;id) = x_i\,p_i^*(\ell;T)}$$

Here x_i is the mole fraction of component-i in the liquid mixture; $\mathrm{p_i^*(\ell;T)}$ is the vapour pressure of pure liquid substance 1 at temperature T.

For example if x_i is 0.5, the contribution to the vapour pressure of the (ideal) mixture is one-half of the vapour pressure of the pure liquid-i at the same temperature. Equation (p) is Raoult's law, describing the properties of an ideal liquid mixture having ideal thermodynamic properties. We note that the Gas Constant emerges in equation (o) because the r.h.s. of equation (o) describes the properties of chemical substance 1 in the vapour phase.

Combination of equations (o) and (p) yields equation (q).

$$\mu_{\mathrm{i}}^{\mathrm{eq}}(\ell;\mathrm{mix;id;T;p}) = \mu_{\mathrm{i}}^*\,(\ \mathrm{g;T;p^0}) + \mathrm{R\,T\,\ln\left[x_i\,p_i^*(\ T)/p^0\right]}$$

$$\mathrm{Or,}\ \mu_{\mathrm{i}}^{\mathrm{eq}}(\ell;\mathrm{mix;id;p;T}) = \mu_{\mathrm{i}}^*\,(\ \mathrm{g;p^0;T}) + \mathrm{R\,T\,\ln\left[p_i^*(\ T)/p^0\right] + R\,T\,\ln\,(x_i)}$$

For the pure liquid-i at pressure p,

$$\mu_{\mathrm{i}}^*(\ell;\mathrm{p;T}) = \mu_{\mathrm{i}}^*\,(\ \mathrm{g;p^0;T}) + \mathrm{R\,T\,\ln\left[p(T)/p^0\right]}$$

$$\mathrm{Hence,}\ \mu_{\mathrm{i}}^{\mathrm{eq}}(\ell;\ \mathrm{mix}\ ;\mathrm{id;p;T}) = \mu_{\mathrm{i}}^*(\ell;\mathrm{p;T}) + \mathrm{R\,T\,\ln\,(x_i)}$$

We notice that the Gas Constant in equation (t) emerged from equation (i) describing the properties of an ideal gas.

Solutions

A similar argument is used when we turn our attention to the thermodynamic properties of a solute, chemical substance j. In this case we use Henry's Law as the link between theory and the properties of solutions. This law relates the equilibrium partial pressure p_j of solute j to the molality of solute j, $\mathrm{m}_j|)for a solution at temperature\backslash(\mathrm{T}$ and pressure p. Experiment shows that certainly for dilute solutions, the partial pressure p_j is close to a linear function of molality m_j. Taking this experimental result as a lead we state that, by definition, in the event that the thermodynamic properties of the solution are ideal, equation (u) relates the partial pressure p_j to the solute molality m_j; $\mathrm{m^0 = 1\ molkg^{-1}}$.

$$\text{Thus, } \mathrm{p_j\,(s\,ln;\,T;\,m_j;\,id) = H_j\,\left(m_j/m^0\right)}$$

Here H_j is Henry's Law constant characteristic of solute, solvent, T and p. H_j is a pressure being the partial pressure of solute j where $\mathrm{m_j = 1\ mol\ kg}$. In other words equation (u) is not thermodynamic in the sense of being derived from the Laws of Thermodynamics. Rather the basis is experiment. We return to equation (n) but written for the equilibrium for solute in solution and in the vapour phase, a mixture of solute j and solvent.

$$\mathrm{\mu_j^{eq}\,(s\,ln;\,m_j;\,T;\,p) = \mu_j^{eq}\left(g;\,mix;\,T;\,p_j^{eq}\right)}$$

For the vapour phase, $\mu_j^{cq}\left(g;\mathrm{mix};T;\mathrm{p_j^{cq}}\right)$ is related to the partial pressure $\mathrm{p_j^{cq}}$ using equation (w).

$$\mathrm{\mu_j^{eq}\left(g;\,mix;\,T;\,p_j^{eq}\right) = \mu_j^0\left(\ g;\,T;\,p^0\right) + R\,T\,\ln\left(p_j^{eq}/p^0\right)}$$

Hence using equations (u)-(w),

$$\mathrm{\mu_j^{cq}\,(s\,ln;\,m_j;\,T;\,p) = \mu_j^0\left(\ g;\,T;\,p^0\right) + R\,T\,\ln\left[\frac{H_j}{p^0}\,\frac{m_j}{m^0}\right]}$$

$$\mathrm{Or,\ \mu_j^{eq}\,(s\,ln;\,m_j;\,T;\,p) = \left\{\mu_j^0\left(\ g;\,T;\,p^0\right) + R\,T\,\ln\left[\frac{H_j}{p^0}\right]\right\} + R\,T\,\ln\left(m_j/m^0\right)}$$

The term $\left\{\mu_j^0\,(g;T;p^0) + RT\,\ln\left[\frac{H_j}{p^0}\right]\right\}$ characterises solute j in a solution at the same T and p when $\mathrm{m_j = 1\ molkg^{-1}}$. Thus we define a reference chemical potential for the solute-j,

$$\mathrm{\mu_j^0(\ s\,ln;\,T;\,p)\ as\ given\ by\ \left\{\mu_j^0(\ g;\,T;\,p) + R\,T\,\ln\left[\frac{H_j}{m_j^0}\right]\right\}}$$

$$\mathrm{Therefore,\ \mu_j^{eq}\,(s\,ln;\,m_j;\,T;\,p) = \mu_j^0(\ s\,ln;\,T;\,p) + R\,T\,\ln\left(m_j/m^0\right)}$$

Again we can trace the gas constant R in equation (za) to a description of the vapour state although the term $\mu_j^{cq}\,(\mathrm{s\,ln;\,m_j;\,T;\,p})$ describes the chemical potential of chemical substance j, the solute, in solution.

Finally we should note that for real as opposed to ideal liquid mixtures and ideal solutions, activity coefficients express the extent to which the properties of these systems differ from those defined as ideal.

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1.5.2: Chemical Potentials- Gases

A given closed system contains gas j at temperature T and pressure p. The chemical potential $\mu_{\mathrm{j}}(\mathrm{g};\mathrm{T};\mathrm{p})$ is given by Equation 1.5.2.1 where p^0 is the standard pressure and $\mathrm{V}_{\mathrm{j}}^*(\ \mathrm{T},\mathrm{p})$ is the molar volume of the gas j.

$$\mu_j(g;T;p) = \mu_j^0(pfg;T) + RT\ln\left(\frac{p}{p^0}\right) + \int_0^p \left[V_j^*(T;p) - \left(\frac{RT}{p}\right)\right] dp \tag{1.5.2.1}$$

$\mathrm{V}_{\mathrm{j}}^*(\ \mathrm{T};\mathrm{p})$ is the molar volume at pressure p and temperature T. In the event that gas j has the properties of a perfect gas, the chemical potential is given by Equation 1.5.2.2.

$$\mu_j(pfg;T;p) = \mu_j^0(pfg;T) + RT\ln\left(\frac{p}{p^0}\right) \tag{1.5.2.2}$$

If gas j exists at mole fraction x_j as one component of a mixture of k gases the chemical potential of gas j is given by Equation 1.5.2.3 where x_{k} is the set of mole fractions defining the composition of the mixture [1].

$$\mu_{\mathrm{j}}\left(\mathrm{g};\mathrm{T};\mathrm{p};\mathrm{x}_{\mathrm{k}}\right) = \mu_{\mathrm{j}}^0(\ \mathrm{g};\mathrm{T}) + \mathrm{RT}\ln\left(\mathrm{x_j p/p}^0\right) + \int_{\mathrm{o}}^{\mathrm{p}} \left[\mathrm{V_j}\left(\mathrm{g};\mathrm{T};\mathrm{p};\mathrm{x_c}\right) - \left(\frac{RT}{p}\right)\right] \mathrm{dp} \tag{1.5.2.3}$$

Here $\mathrm{V_j}\left(\mathrm{g};\mathrm{T};\mathrm{p};\mathrm{x_c}\right)$ is the molar volume of gas j in the gaseous mixture.

Footnote

[1] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979, page 184.

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1.5.3: Chemical Potentials- Solutions- General Properties

A key quantity in chemical thermodynamics is the chemical potential of chemical substance j, μ_j. The latter is the differential dependence of Gibbs energy on amount of substance j at fixed T, p and amounts of all other substances in the system [1].

$$\mu_{\mathrm{j}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}}$$

An important point to note is that the conditions 'fixed T and fixed p' on the partial differential refer to intensive variables. These conditions are called Gibbsian in recognition of the development by Gibbs of the concept of thermodynamic potential for changes in the properties of a closed system at fixed T and fixed p.

In general terms, the chemical potential of substance j is defined using analogous partial derivatives of the thermodynamic internal energy U, enthalpy H and Helmholtz energy F.

$$\mu_{\mathrm{j}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{n_j}}\right)_{\mathrm{s,V,n(i\neq j)}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{n_j}}\right)_{\mathrm{s,p,n(i\neq j)}} = \left(\frac{\partial \mathrm{F}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,V,n(i\neq j)}}$$

With reference to a given closed system, thermodynamics defines macroscopic properties including volume V, Gibbs energy G, enthalpy H and entropy S. Nevertheless we need to "tell" these thermodynamic variables that a given system probably comprises different chemical substances. The analysis is reasonably straightforward if we define the system under consideration by the 'Gibbsian' set of independent variables; i.e. T, p and amounts of each chemical substance [2]. The analysis leads to the definition of a chemical potential for each substance j, μ_j, in a closed system [3,4].

Footnotes

[1] It might be argued that we have switched our attention from closed to open systems because we are considering a change in Gibbs energy when we add ∂n_j moles of substance to the system. This comment is true in part. But what we actually envisage is something a little different. We take a closed system containing n_1 and n_j moles of substances 1 and j respectively. We open the system, rapidly pop in $\delta \mathrm{n_j}$ moles of substance j and put the lid back on the system to return it to the closed state. Then the closed system contains $(\mathrm{n_j} + \delta \mathrm{n_j})$ moles of substance j so changes in chemical composition and molecular organisation follow producing a change in Gibbs energy at, say, fixed T and fixed p.

[2] G. N. Lewis, (with possibly one of the key papers in chemistry)

a. Z.Phys.Chem.,1907,**61**,129.
b. Proc. Acad. Arts Sci.,1907,**43**,259.

[Comment: Paper (a) is the German translation of paper (b).]

[3] The analysis presented here (a) is confined to bulk systems in the absence of magnetic and electric fields and (b) ignores surface effects.

[4] To quote E. Grunwald [J. Am. Chem. Soc., 1984, **106**, 5414] "any first derivative with respect to any variable of state at equilibrium is isodelphic"; see also E. Grunwald, Thermodynamics of Molecular Species, Wiley, New York, 1997.

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1.5.4: Chemical Potentials- Solutions- Composition

A given aqueous solution at temperature T and pressure p (both near ambient) was prepared using n_1 moles of water and n_j moles of urea (i.e. chemical substance j). The Gibbs energy $\mathrm{G(aq)}$, an extensive property (variable), is given by the sum of products of amounts of each chemical substance and chemical potentials [1].

$$\mathrm{G(aq) = n_1\,\mu_1(aq) + n_j\,\mu_j(aq)} \tag{1.5.4.1}$$

Equation 1.5.4.1 is key although we cannot put number values to $\mathrm{G(aq)}$, $\mu_1\mathrm{(aq)}$ and $\mu_j\mathrm{(aq}$. The latter two quantities are, respectively, the chemical potentials of the solvent, water and solute j in the aqueous solution at the same temperature and pressure. Equation 1.5.4.1 seems a strange starting point granted it contains three quantities which we can never know. Matters can only improve.

There is merit in turning attention to an intensive property describing the Gibbs energy of a solution prepared using $1\ \mathrm{kg}$ of solvent, $\mathrm{G\,(aq;\,w_1 = 1.0\ kg)}$. Therefore, we do not have to worry about the size of the flask containing the solution. The same descriptor applies to $0.1\ \mathrm{cm^3}$ or $10\mathrm{m^3}$ of a given solution [2,3].

$$\text{By definition} \quad \mathrm{G\,(aq;\,w_1 = 1.0\ kg) = G(aq)/w_1}$$

$$\mathrm{G\,(aq;\,w_1 = 1.0\ kg) = (1/M_1)\ \mu_1(aq) + m_j\,\mu_j(aq)}$$

$\mathrm{M_1}$ is the molar mass of solvent, water, and mj is the molality of solute j. Again we cannot put number values to $\mathrm{G\,(aq;\,w_1 = 1.0\ kg)}$, $\mu_1\mathrm{(aq)}$ and $\mu_j\mathrm{(aq)}$. Faced with this situation, the well-established approach involves an examination of differences. With respect to $\mu_1(aq)$, the properties of water in an aqueous solution are compared with the properties of water at the same temperature and pressure. In these terms, we compare $\mu_1(\mathrm{aq, T, p})$ with $\mu_1^*(\ell, T, p)$. The superscript * in the latter term indicates that the chemical substance is pure and the symbol 'ℓ indicates that this substance is a liquid. Hence, comparison is drawn with the chemical potential of pure liquid water at the same T and p. In one sense we regard the solute as a controlled impurity perturbing the properties of the solvent. [We use the subscript '1' to indicate chemical substance 1 which in the convention used here refers to the solvent; water in the case of aqueous solutions.]

In considering the properties of, for example, urea in this aqueous solution molality m_j, we need a reference state against which to compare the properties of urea in the real solution prepared by dissolving n_j moles of urea in n_1 moles of water. There is little point in comparing the properties of solute, urea with those of solid urea, a hard crystalline solid. Instead, we identify a reference solution state.

In general terms chemists explore how the chemical potentials of solvent and solute in an aqueous solution are related to the composition of the solution. Equations which offer such relationships should satisfy two criteria [4]: in the limit of infinite dilution (i) the partial molar volumes $\mathrm{V_j(aq)}$ and $\mathrm{V_1(aq)}$ are meaningful and (ii) the partial molar enthalpies $\mathrm{H_j(aq}$ and $\mathrm{H_1(aq)}$ are meaningful. In other words, these properties do not approach an asymptotic limit of either $+\infty$ or $-\infty$ with increasing dilution. For this reason physical chemists usually favour expressing the composition of solutions in molalities.

In summary analysis of the properties of solutions and liquid mixtures is built around the somewhat abstract concept of the chemical potential introduced by J. Willard Gibbs and by Pierre Duhem. The task of showing chemists the significance and application of this concept was left to Lewis and Randall in their classic monograph [5] published in 1923 [6]. Chemical potentials are one example of a class of properties called partial molar which provide the key link between macroscopic thermodynamic descriptions of systems and molecular properties [7].

Footnotes

[1] $\mathrm{G(aq) = [mol]\ [Jmol^{-1}] + [mol]\ [Jmol^{-1}] = [J]}$

[2] $\mathrm{G\,(aq;\,w_1 = 1.0\ kg) =}$
$\mathrm{[1/kgmol^{-1}]\ [Jmol^{-1}] + [molkg^{-1}]\ [Jmol^{-1}] = [Jkg^{-1}]}$

[3] With reference to equations (a) and (c), we must avoid the temptation to write “at constant temperature and pressure”. This condition is implicit in the description of the system using the independent variables $\mathrm{[T, p, n_1, n_j]}$ for the aqueous solution containing the solute with the added condition that T and p are intensive variables; i.e. the set of independent variables is Gibbsian. Nonetheless there is often merit in using a complete set of descriptions of a system even if we over-define the variable under discussion. In describing the Gibbs energy defined by equation (a), we might write $\mathrm{G(T; p; aq)}$. Similarly for the system described

by equation (b) it is often helpful to write $\mathrm{G\,(T;p;aq;w_1 = 1\ kg;m_j)}$. In reviewing the properties of solutions our interest, unless otherwise stated, centres on solutions at equilibrium where the affinity A is zero and the organisation characteristic of the equilibrium system, ξ^{eq}. We may find it helpful to write $\mathrm{G\,(T;p;aq;w_1 = 1\ kg;m_j;A = 0;\xi^{eq})}$, replacing G by H, S and V for the corresponding enthalpy, entropy and volume of this solution. Clearly this over-definition is somewhat silly. Nevertheless it is often preferable to over-define a system rather than under-define when mistakes can arise.

[4] J. E. Garrod and T. M. Herrington, J. Chem. Educ., 1969, **46**, 165.

[5] G. N. Lewis and M. L. Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill, New York, 1923.

[6] See also, G. N. Lewis, Proc. Am. Acad. Arts Sci.,1907,**43**,259.

[7] L. Hepler, Thermochim. Acta, 1986, **100**, 171.

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1.5.5: Chemical Potentials- Solutions- Partial Molar Properties

A given solution comprises $\mathrm{n_1}$ moles of solvent, liquid chemical substance 1, and $\mathrm{n_j}$ moles of solute, chemical substance j. We ask ---- What contributions are made by the solvent and by the solute to the volume of the solution at defined T and p? In fact we can only guess at these contributions. This is disappointing. The best that we can do is to probe the sensitivity of the volume of a given solution to the addition of small amounts of solute and of solvent. This approach leads to a set of properties called partial molar. The starting point is the Gibbs energy of a solution. We develop an argument which places the Gibbs energy at the centre from which all other thermodynamic variables develop.

A given closed system comprises $\mathrm{n_1}$ moles of solvent (e.g. water) and $\mathrm{n_j}$ moles of a simple solute j (e.g. urea) at temperature T and pressure p. The Gibbs energy of the solution is defined by equation (a).

$$\mathrm{G} = \mathrm{G}\left[\mathrm{T}, \mathrm{p}, \mathrm{n_l}, \mathrm{n_j}\right] \tag{1.5.5.1}$$

We introduce a partial derivative having the following form: $\left(\frac{\partial G}{\partial n_j}\right)_{T,p,n_1}$. The latter partial differential describes the differential dependence of Gibbs energy G on the amount of chemical substance j. By definition, the chemical potential of chemical substance j,

$$\mu_{\mathrm{j}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n_l}}$$

We also envisage that displacement of the system by adding δn_j moles of chemical substance j from the original state to a neighbouring state produces a change in Gibbs energy at temperature T and pressure p. In one class of displacements the system moves along a path of constant affinity for spontaneous reaction A. In another displacement the system moves along a path at constant organisation/composition, ξ; i.e. frozen. These two pathways are related by the following equation. For the system at fixed T, p and $\mathrm{n_1}$

$$\left[\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right]_{\mathrm{A}} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right]_{\xi} - \left[\frac{\partial \mathrm{A}}{\partial \mathrm{n_j}}\right]_{\xi}\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{n(j)}}\left[\frac{\partial \mathrm{G}}{\partial \xi}\right]_{\mathrm{n(j)}}$$

The conditions, constant T and p, refer to intensive variables. We direct attention to a closed system at equilibrium where '$\mathrm{A} = 0$' and the composition $\xi = \xi^{\mathrm{eq}}$. Moreover at equilibrium, $(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}}$ is zero. Therefore the chemical potential of chemical substance j in a system at equilibrium is defined by the following equation. Hence from equation (c),

$$\mu_{\mathrm{j}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n_1,\ A=0}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n_1,,G^{eq}}}$$

A similar argument in the context of chemical substance 1 shows that,

$$\mu_1 = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_1}}\right)_{\mathrm{T,p,n_j,A=0}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_1}}\right)_{\mathrm{T,p,n_j,\zeta^{eq}}}$$

Equations (d) and (e) are key results. Similarly for a closed system at equilibrium at fixed T and fixed p (at a minimum in G, $\mathrm{A} = 0$, $\xi = \xi^{\mathrm{eq}}$), for all i-substances,

$$V_j(A = 0) = V_j\left(\xi^{eq}\right)$$

$$\mathrm{S_j}(\mathrm{A} = 0) = \mathrm{S_j}\left(\xi^{\mathrm{eq}}\right)$$

$$\mathrm{H_j}(\mathrm{A} = 0) = \mathrm{H_j}\left(\xi^{eq}\right)$$

$$\mu_j(A = 0) = \mu_j\left(\xi^{eq}\right)$$

But in the case of, for example, isobaric expansions and isobaric heat capacities, $\mathrm{E_{pj}}(\mathrm{A} = 0) \neq \mathrm{E_{pj}}\left(\xi^{\mathrm{eq}}\right)$ and $\mathrm{C_{pj}}(\mathrm{A} = 0) \neq \mathrm{C_{pj}}\left(\xi^{eq}\right)$. The identifications, (f) to (i), arise because these variables are first derivatives of the Gibbs energy of a closed system at equilibrium where $(\partial \mathrm{G}/\partial \xi)$ at fixed T and p is zero.

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1.5.6: Chemical Potentials- Liquid Mixtures- Raoult's Law

A given closed system contains two volatile miscible liquids. The closed system is connected to a pressure-measuring device which records that at temperature T the pressure is ptot. The composition of the liquid mixture is known; i.e. mole fractions $\mathrm{x_1}$ and $\mathrm{x_2}$ (where $\mathrm{x_2 = 1 - x_1}$). The system contains two components so that in terms of the Phase Rule, $\mathrm{C = 2}$ There are two phases, vapour and liquid so that $\mathrm{P = 2}$. From the rule, $\mathrm{P + F = C + 2}$, we have fixed the composition and temperature using up the two degrees of freedom. Hence the pressure ptot is fixed.

We imagine that the mixture under examination is a binary aqueous mixture; water is chemical substance 1. If we measure the partial pressure of, say, liquid 1, $\mathrm{p_1}$ we find that $\mathrm{p_1}$ is close to a linear function of mole fraction $\mathrm{x_1}$.

$$\text{At equilibrium and temperature T,} \quad \mathrm{p_1^{eq} \cong p_1^*(\ell)\, x_1}$$

As the mole fraction $\mathrm{x_1}$ approaches unity (i.e. the composition of the mixture approaches pure water) the equilibrium vapour pressure of water $\mathrm{p_1^{eq}}$ approaches that of pure liquid water at the same temperature, $\mathrm{p_1^*(\ell)}$ We have linked the equilibrium **vapour** pressure of water to the composition of the **liquid** mixture.

In fact it turns out that as the composition of the mixture approaches pure liquid 1, the latter relationship becomes an equation. We assert that if the thermodynamic properties of the mixture were ideal then $\mathrm{p_1}$ would be related to mole fraction $\mathrm{x_1}$ using the following equation.

$$\mathrm{p_1(mix; id) = x_1\, p_1^*(\ell)}$$

Returning to experiment, we invariably find that as a real solution becomes more dilute (i.e. as $\mathrm{x_1}$ approaches unity) $\mathrm{p_1^{eq}}$ for real solutions approaches $p_1^{eq}(aq; id)$. Therefore we rewrite equation (b) as an equation for a real solution by introducing a new property called the (rational) activity coefficient $\mathrm{f_1}$.

$$\mathrm{p_1(mix) = x_1\, f_1\, p_1^*(\ell)}$$

Here $\mathrm{f_1}$ is the (rational) activity coefficient for liquid component 1 defined as follows.

$$\text{limit}\,(x_1 \to 1)\, f_1 = 1$$

$$\text{Similarly for volatile liquid 2;}\, p_2 = x_2\, f_2\, p_2^*$$

$$\text{limit}\,(x_2 \to 1)\, f_2 = 1$$

Although equations (d) and (f) have simple forms, rational activity coefficients carry a heavy load in terms of information. For a given aqueous system, $\mathrm{f_1}$ describes the extent to which interactions involving water molecules in a real system differ from those in the corresponding ideal system. The challenge of expressing this information in molecular terms is formidable.

We carry over these ideas to the task of formulating an equation for the chemical potential of water in the liquid mixture at temperature T and pressure p. We make the link between partial pressure and the tendency for liquid 1 to escape to the vapour phase, down a gradient of chemical potential

By definition (at temperature T and pressure p),

$$\mathrm{\mu_1(mix) = \mu_1^*(\ell) + R\,T\,\ln(x_1\, f_1)}$$

$$\text{where, at all T and p,} \quad \mathrm{\text{limit}\,(x_1 \to 1.0)\, f_1 = 1.0}$$

$\mathrm{\mu_1^*(\ell)}$ l is the chemical potential of pure liquid water (at the same T and p). In other words, pure liquid water is the reference state against which we compare the properties of water in an aqueous mixture. For the pure liquid at temperature T, $V_1^*(\ell) = \mathrm{d\mu_1^*(\ell)/dp}$. If $\mathrm{p^0}$ is the standard pressure [1] $\left(10^5\ \mathrm{N\ m^{-2}}\right)$,

$$\mathrm{\int_{p^0}^{p} d\mu_1^*(\ell) = \int_{p^0}^{p} V_1^*(\ell)\, dp}$$

$$\text{Then [2],} \quad \mathrm{\mu_1^*(\ell; T; p) - \mu_1^0(\ell; T) = \int_{p^0}^{p} V_1^*(\ell)\, dp}$$

$\mu_1^0(\ell;\mathrm{T})$ is the standard chemical potential of water(ℓ) at temperature T.

$$\text{Therefore,} \quad \mu_1(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_1^0(\ell;\mathrm{T}) + \mathrm{R\,T\,ln\,(x_1\,f_1)} + \int_{\mathrm{p}^0}^{\mathrm{p}} \mathrm{V}_1^*(\ell)\,\mathrm{dp}$$

This is an important equation although, at this stage, we can go no further. Without information concerning the dependence on pressure of $\mathrm{V}_1^*(\ell)$ {or density} we cannot evaluate the integral in equation (k). However, we can comment on possible patterns in these chemical potentials. If the thermodynamic properties of the liquid mixture are ideal then $\mathrm{f_1}$ equals 1.0. Hence equation (k) takes the following simple form (at fixed T and p).

$$\mu_1(\mathrm{mix};\mathrm{id}) = \mu_1^*(\ell) + \mathrm{R\,T\,ln\,(x_1)}$$

In a solution the mole fraction x1 is less than unity and so $\ln(x_1) < 0$ [3]. Hence $\mu_1(\mathrm{mix};\mathrm{id}) < \mu_1^*(\ell)$ at the same T and p [4]

Footnotes

[1] J.D. Cox, Pure Appl. Chem., 1982,**54**, 1239; R.D. Freeman, Bull. Chem. Thermodyn., 1982,**25**, 523.

[2] $\mathrm{V}_1^*(\ell)\,\mathrm{dp} = \left[\mathrm{m^3\ mol^{-1}}\right]\ \left[\mathrm{Nm^{-2}}\right] = \left[\mathrm{Nmmol^{-1}}\right] = \left[\mathrm{Jmol^{-1}}\right]$

[3] With increase in the amount of component 2 so $\mathrm{x_1}$ tends to zero. In this limit $\mu_1(\mathrm{aq})$ is minus infinity.

[4] Note that $\mathrm{p}_1^{\mathrm{eq}}(\mathrm{mix};\mathrm{id}) - \mathrm{p}_1^* < 0$. Adding a solute lowers the vapour pressure of the water. However the total vapour pressure of a binary liquid mixture can be either increased or decreased by adding a small amount of the second component; G. Bertrand and C. Treiner, J. Solution Chem.,1984,**13**,43.

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1.5.7: Chemical Potentials- Solutions- Raoult's Law

A given closed system contains an aqueous solution; the solute is chemical substance j. The system is at equilibrium at temperature T. The chemical potential of water in the aqueous solution is related to the mole fraction $\mathrm{x_1}$ of water using equation (a) which is based on **Raoult's Law** for the solvent.

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^0(\ell;\mathrm{T}) + \mathrm{R\,T\,\ln(x_1\,f_1)} + \int_{\mathrm{p^0}}^{\mathrm{p}} \mathrm{V_1^*}(\ell)\,\mathrm{dp}$$

$$\text{By definition, at all T and p, limit}\,(\mathrm{x_1} \rightarrow 1)\,\mathrm{f_1} = 1$$

If ambient pressure is close to the standard pressure $\mathrm{p^0}$, the chemical potential of solvent water in the aqueous solution is given by equation (c).

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^0(\ell;\mathrm{T}) + \mathrm{R\,T\,\ln(x_1\,f_1)}$$

For an ideal solution, $\mathrm{f_1} = 1$.

$$\mu_1(\mathrm{aq;T;p;id}) = \mu_1^0(\ell;\mathrm{T}) + \mathrm{R\,T\,\ln(x_1)}$$

But for a solution $\mathrm{x_1} < 1.0$ and so $\ln(x_1) < 0$. In other words, by adding a solute to water (forming an ideal solution) we stabilise the solvent. We define a quantity $\Delta(\ell \rightarrow aq)\mu_1(\ \mathrm{T,p})$ using equation (e) which measures the change in chemical potential of water when one mole of water is transferred from water(ℓ) to an ideal aqueous solution.

$$\Delta(\ell \rightarrow \mathrm{aq})\mu_1(\ \mathrm{T,p}) = \mu_1(\mathrm{aq}) - \mu_1^*(\ell) = \mathrm{R\,T\,\ln(x_1)}$$

i.e. $\Delta(\ell \rightarrow \mathrm{aq})\mu_1(\ \mathrm{T,p;id}) < 0$

In the case of a real solution, the extent of stabilisation depends on whether $\mathrm{f_1}$ is either larger or smaller than unity. [Note that $\mathrm{f_1}$ cannot be negative]. This line of argument leads to an important theme in the description of the properties of aqueous solutions. We compare the chemical potentials of water in real and in the corresponding ideal solutions. The difference is the excess chemical potential, $\mu_1^E(aq;T;p)$.

$$\text{By definition,} \quad \mu_1^{\mathrm{E}}(\mathrm{aq;T;p}) = \mu_1(\mathrm{aq;T;p}) - \mu_1(\mathrm{aq;T;p;id})$$

$$\text{Hence} \quad \mu_1^{\mathrm{E}}(\mathrm{aq;T;p}) = \mathrm{R\,T\,\ln(f_l)}$$

If $\mathrm{f_1} > 1.0$, then $\mu_1^{\mathrm{E}}(\mathrm{aq;T;p}) > 0$; if $\mathrm{f_1} < 1.0$, then $\mu_1^{\mathrm{E}}(\mathrm{aq;T;p}) < 0$. In the latter case, interactions involving solute and solvent are responsible for the fact that the properties of a given solution are not ideal and the fact that these interactions stabilise the solvent relative to that for an ideal solution.

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1.5.8: Chemical Potentials- Solutions- Osmotic Coefficient

The chemical potential of (solvent) water in an aqueous solution can be related to the mole fraction composition of the solution. However, there is a possible disadvantage in an approach using the mole fraction scale to express the composition of a solution. We note that our interest is often in the properties of solutes in aqueous solutions, that the amount of solvent greatly exceeds the amount of solute in a solution, and that the sensitivity of equipment developed by chemists is sufficient to probe the properties of quite dilute solutions. Consequently the mole fraction scale for the solvent is not the most convenient method for expressing the composition of a given solution [1]. Hence another equation relating $\mu_1(\mathrm{aq;T;p})$ to the composition of a solution finds favour. By definition, for a solution containing a single solute, chemical substance j, [2],

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^*(\ell;\mathrm{T;p}) - \phi\,\mathrm{R\,T\,M_1\,m_j}$$

In terms of the standard chemical potential for water at temperature $|mathrmT$,

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^*(\ell;\mathrm{T;p}) - \phi\,\mathrm{R\,T\,M_1\,m_j}$$

$\mathrm{M_1}$ is the molar mass of water; ϕ is the practical osmotic coefficient which is characteristic of the solute, molality m_j, temperature and pressure. By definition, ϕ is unity for ideal solutions at all temperatures and pressures.

$$\mathrm{limit\,(m_j \to 0)}\;\phi = 1.0 \text{ at all T and p}$$

Further for ideal solutions, the partial differentials $(\partial\phi/\partial\mathrm{T})_\mathrm{p}$, $(\partial^2\phi/\partial T^2)_p$ and $(\partial\phi/\partial\mathrm{p})_\mathrm{T}$ are zero.

$$\text{For an ideal solution [3]},\quad \mu_1(\mathrm{aq;T;p;id}) = \mu_1^*(\ell;\mathrm{T;p}) - \mathrm{R\,T\,M_1\,m_j}$$

We rewrite equation (d) in the following form:

$$\mu_1(\mathrm{aq;T;p;id}) - \mu_1^*(\ell;\mathrm{T;p}) = -\mathrm{R\,T\,M_1\,m_j}$$

Hence with an increase in molality of solute in an ideal aqueous solution, the solvent is stabilised, being at a lower chemical potential than that for pure water(ℓ).We contrast the chemical potentials of the solvent in real and ideal solutions using an excess chemical potential, $\mu_1^\mathrm{E}(\mathrm{aq;T;p})$;

$$\begin{aligned}\mu_1^\mathrm{E}(\mathrm{aq;T;p}) = \mu_1(\mathrm{aq;T;p}) - \mu_1(\mathrm{aq;id;T;p}) \\ = (1-\phi)\,\mathrm{R\,T\,M_1\,m_j}\end{aligned}$$

The term $(1-\phi)$ is often encountered because it expresses succinctly the impact of a **solute** on the properties of a solvent. At a given molality (and fixed temperature and pressure), ϕ is characteristic of the solute.

Footnote

[1] Mole fractions of solvent $\mathrm{x_1}$ and solute x_j for aqueous solutions having gradually increasing molality of solute m_j.

a. $\mathrm{m_j/molkg^{-1}} = 10^{-3}$; $\mathrm{x_1} = 0.999982$ $\mathrm{x_j} = 1.8\times10^{-5}$
b. $\mathrm{m_j/molkg^{-1}} = 10^{-2}$; $\mathrm{x_1} = 0.99982$ $\mathrm{x_j} = 1.8\times10^{-4}$
c. $\mathrm{m_j/molkg^{-1}} = 10^{-1}$; $\mathrm{x_1} = 0.9982$ $\mathrm{x_j} = 1.8\times10^{-3}$
d. $\mathrm{m_j/molkg^{-1}} = 0.5$; $\mathrm{x_1} = 0.9911$ $\mathrm{x_j} = 8.9\times10^{-3}$
e. $\mathrm{m_j/molkg^{-1}} = 1.0$; $\mathrm{x_1} = 0.9823$ $\mathrm{x_j} = 1.77\times10^{-2}$

[2] $\begin{aligned}&[\mathrm{Jmol^{-1}}] = \\ &[\mathrm{Jmol^{-1}}] - [1]\ [\mathrm{JK^{-1}\ mol^{-1}}]\ [\mathrm{K}]\ [\mathrm{kgmol^{-1}}]\ [\mathrm{molkg^{-1}}]\end{aligned}$

[3] The definitions of ideal solutions expressed here and in terms of mole fraction of solvent are not in conflict. For an ideal solution these equations require that, $-\mathrm{M_1\,m_j} = \ln(\mathrm{x_1})$
But $\ln(\mathrm{x_1}) = \ln\left[\mathrm{M_1^{-1}}/\left(\mathrm{M_1^{-1}} + \mathrm{m_j}\right)\right] = -\ln(1.0 + \mathrm{m_j\,M_1})$
Bearing in mind that $\mathrm{M_1} = 0.018\ \mathrm{kg\ mol^{-1}}$, for dilute solutions $\ln(1.0 + \mathrm{m_j\,M_1}) = \mathrm{m_j\,M_1}$.

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1.5.9: Chemical Potentials; Excess; Aqueous Solution

A given aqueous solution, at temperature T and pressure p ($\cong \mathrm{p}^0$), contains a solute, chemical substance j. If the thermodynamic properties of the solution are ideal, the chemical potential of the solute is given by equation (a).

$$\mu_{\mathrm{j}}(\mathrm{aq};\mathrm{id}) = \mu_{\mathrm{j}}^0(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}/\mathrm{m}^0\right)$$

For the corresponding real solution,

$$\mu_{\mathrm{j}}(\mathrm{aq}) = \mu_{\mathrm{j}}^0(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^0\right)$$

Here γ_j is the activity coefficient. The excess chemical potential, $\mu_{\mathrm{j}}^{\mathrm{E}}(\mathrm{aq})$ is given by equation (c).

$$\mu_{\mathrm{j}}^{\mathrm{E}}(\mathrm{aq}) = \mu_{\mathrm{j}}(\mathrm{aq}) - \mu_{\mathrm{j}}(\mathrm{aq};\mathrm{id})$$

$$\text{Then, } \mu_j^E(aq) = RT\,\ln(\gamma_j)$$

Often an excess chemical potential $\mu_{\mathrm{j}}^{\mathrm{E}}(\mathrm{aq})$ is written in the form $\mathrm{G}_j^{\mathrm{E}}$. The latter notation stems from the fact that chemical potentials are partial molar Gibbs energies. In the case of the solvent, water(ℓ), the corresponding equations for the chemical potentials in solutions having either ideal or real thermodynamic properties are given by equations (e) and (f).

$$\mu_1(\mathrm{aq};\mathrm{id}) = \mu_1^*(\ell) - \mathrm{R\,T\,M_1\,m_j}$$

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - \phi\,\mathrm{R\,T\,M_1\,m_j}$$

$$\mu_1^{\mathrm{E}}(\mathrm{aq}) = (1-\phi)\,\mathrm{R\,T\,M_1\,m_j}$$

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1.5.10: Chemical Potentials- Solutions- Henry's Law

A given aqueous solutions at temperature T contains a simple solute j, molality m_j. Experiment shows that at equilibrium the partial pressure p_j is close to a linear function of molality m_j, the constant of proportionality being the Henry's Law constant for this particular solute in a defined solvent; equation(a).

$$\mathrm{p_j} \cong \mathrm{H_j}\ \left(\mathrm{m_j}/\mathrm{m}^0\right)$$

By definition $\mathrm{m}^0 = 1.0\ \mathrm{mol\ kg}^{-1}$. Experiment shows that as a given real solution becomes more dilute so the relationship given in (a) can be written as an equation. The relationship in (a) is rewritten as an equation to describe the properties of a solution having thermodynamic properties which are ideal.

$$p_j(\mathrm{id}) = \mathrm{H_j}\ \left(\mathrm{m_j}/\mathrm{m}^0\right)$$

In other words H_j is the partial pressure of volatile solute in a solution having thermodynamic properties which are ideal and where the molality of the solute equals $1.0\ \mathrm{molkg}^{-1}$.

For a real solution at equilibrium and at temperature T, the partial pressure $\mathrm{p_j(\ real\ )}$ is related to molality mj using equation (c) where γ_j is the activity coefficient describing the properties of solute j in solution

$$\mathrm{p_j(\ real\ )} = \mathrm{H_j}\ \left(\mathrm{m_j}/\mathrm{m}^0\right)\ \gamma_\mathrm{j}$$

$$\mathrm{By\ definition,\ at\ all\ T\ and}\ p\,\mathrm{lim\,it}\,(\mathrm{m_j} \rightarrow 0)\,\gamma_\mathrm{j} = 1$$

As m_j decreases so $\mathrm{p_j(\ real\ )}$ approaches $\mathrm{p_j(id)}$.

Henry's Law forms the basis of equations which are used to related the chemical potential of solute j, μ_j to the composition of a solution.

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1.5.11: Chemical Potentials- Solutes

A given aqueous solution is prepared using $1\ \mathrm{kg}$ of water at temperature T and pressure p. The molality of solute j is m_j. The chemical potential of solute j, $\mu_\mathrm{j}(\mathrm{aq};\mathrm{T};\mathrm{p})$ is related to m_j using equation (a).

$$\mu_\mathrm{j}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_\mathrm{j}^0(\mathrm{aq};\mathrm{T}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_\mathrm{j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right) + \int_{\mathrm{p}^a}^{\mathrm{p}} \mathrm{V}_\mathrm{j}^\infty(\mathrm{aq};\mathrm{T})\,\mathrm{dp}$$

$$\text{By definition, } \lim\left(\mathrm{m}_\mathrm{j} \to 0\right)\gamma_\mathrm{j} = 1.0$$

$\mu_j^0(\mathrm{aq};\mathrm{T})$ is the chemical potential of solute j in an ideal solution (where $\gamma_j = 1$) at temperature T and standard pressure $\mathrm{p}^0\ \left[= 10^5\ \mathrm{Pa}\right]$.

For solutions at ambient pressure which is close to p^0, $\mu_\mathrm{j}(\mathrm{aq};\mathrm{T};\mathrm{p})$ is related to m_j using equation (c).

$$\mu_j(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_\mathrm{j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)$$

Henry's law forms the basis of equations (a) and (c).

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1.5.12: Chemical Potentials- Solute; Molality Scale

A given aqueous solution comprises $\mathrm{n_1}$ moles of solvent (e.g. water) and n_j moles of solute (e.g. urea) at equilibrium, temperature T and pressure p. Thus the molality of solute j is given by equation (a).

$$\mathrm{m_j = n_j/w_1 = n_j/n_1\,M_1}$$

$$\mu_j(\mathrm{aq;T;p}) = \mu_\mathrm{j}^0\,(\mathrm{aq;T;p^0}) + \mathrm{R\,T\,\ln\left(m_j\,\gamma_j/m^0\right)} + \int_{\mathrm{p^0}}^{\mathrm{p}} \mathrm{V_j^\infty(aq)\,dp}$$

i. $\mu_j(aq;T;p)$ = chemical potential of solute j in solution.
ii. $\mu_\mathrm{j}^0(\mathrm{aq;T;p})$ = chemical potential of solute j in the corresponding ideal solution (where $\gamma_j = 1.0$) at temperature T where $\mathrm{m}_j = 1\ \mathrm{molkg^{-1}}$ and where the pressure is the standard pressure $\mathrm{p^0}$.
iii. $\mathrm{m^0 = 1\ mol\ kg^{-1}}$
iv. $\mathrm{V_j^\infty(aq)}$ is the limiting partial molar volume of solute j at temperature T.
v. By definition, $\mathrm{limit\,(m_j \to 0)\,\gamma_j = 1}$ at all T and p.

Activity coefficient γ_j takes account of the fact that the thermodynamic properties of real solutions are not ideal [1]. An important consideration in understanding the factors which affect γ_j is the distance between solute molecules in solution. As we dilute the solution such that m_j approaches zero so inter solute distances approache infinity; i.e. in the limit of infinite dilution or zero molality.

If pressure is ambient and hence close to the standard pressure the integral term in equation (b) is negligibly small.

$$\mathrm{Hence,\ }\mu_\mathrm{j}(\mathrm{aq;T;p}) = \mu_\mathrm{j}^0(\mathrm{aq;T}) + \mathrm{R\,T\,\ln\left(m_j\,\gamma_j/m^0\right)}$$

At this stage we focus attention on the activity coefficient γ_j. We start with equation (c) and by split the logarithm term. For solutions where the pressure p is close to the standard pressure $\mathrm{p^0}$

$$\mu_\mathrm{j}(\mathrm{aq;T;p}) = \mu_\mathrm{j}^0(\mathrm{aq;T}) + \mathrm{R\,T\,\ln\left(m_j/m^0\right)} + \mathrm{R\,T\,\ln\left(\gamma_j\right)}$$

If the properties of the solution are ideal, equation (c) takes the following form.

$$\mu_j(\mathrm{aq;id;T;p}) = \mu_\mathrm{j}^0(\mathrm{aq;T}) + \mathrm{R\,T\,\ln\left(m_j/m^0\right)}$$

If $\mathrm{m_j < 1.0\ mol\ kg^{-1}, R\ T\ \ln\left(m_j/m^0\right)}$ is < 0. $\mu_j(\mathrm{aq;id;T;p}) < \mu_\mathrm{j}^0(\mathrm{aq;T})$. Solute-$j$ is stabilised relative to solute j in the solution reference state, an ideal solution having unit molality. If $\mathrm{m_j > 1.0\ mol\ kg}$, $\mathrm{R\ T\ \ln\left(m_j/m^0\right)}$ is $>$ zero. Hence, $\mu_\mathrm{j}(\mathrm{aq;id;T;p}) > \mu_\mathrm{j}^0(\mathrm{aq;T})$; solute-$j$ is destabilised relative to solute j in the (ideal) solution reference state.

We also compare the chemical potentials of solute j in real and ideal solutions at the same molality leading to the definition of an excess chemical potential for solute j, $\mu_\mathrm{j}^\mathrm{E}(\mathrm{aq})$.

$$\mu_j^\mathrm{E}(\mathrm{aq}) = \mu_j(\mathrm{aq}) - \mu_\mathrm{j}(\mathrm{aq;id})$$

$$\mathrm{Hence,\ }\mu_\mathrm{j}^\mathrm{E}(\mathrm{aq}) = \mathrm{R\,T\,\ln\left(\gamma_j\right)}$$

$$\mathrm{where\ \ lim\,it\,(m_j \to 0)\,\gamma_j = 1\ and\ \ln\left(\gamma_j\right) = 0\ at\ all\ T\ and\ p.}$$

Equation (g) highlights the role played by activity coefficient γ_j; γ_j can be neither zero nor negative; the range for γ_j is from below to above unity. In contrast $\ln\left(\gamma_j\right)$ can be zero (as in an ideal solution) and be either greater or less than zero.

Activity coefficients are interesting quantities. For a given solute j at molality m_j in an aqueous solution (at fixed temperature and pressure) γ_j describes the impact on the chemical potential $\mu_j(\mathrm{aq})$ of solute - solute interactions. The basis of this conclusion follows from the definition given in equation (h) [3]. As a solution is diluted, so the mean distance of separation of solute molecules increases. In these terms a model for an ideal solution, molality mj is one in which each solute molecule contributes to the properties of a given solution independently of all other solutes in the system. In an operational sense, each solute molecule in unaware of the presence of other solute molecules in solution and in these terms the solute molecules are infinitely far apart.

We emphasise the point that activity coefficient γ_j is an interesting and important quantity; γ_j describes the impact on chemical potential $\mu_j(\mathrm{aq;T;p})$ of solute - solute interactions. These interactions can be cohesive (i.e. attractive) such that $\gamma_j < 1, \ln(\gamma_j) < 0$ and $\mu_j(\ \mathrm{aq}\ ;\ \mathrm{real};\ T;p) < \mu_j(\ \mathrm{aq;ideal};\ T;p)$, a stabilising influence. On the other hand, solute - solute interactions may be repulsive. In view of the fact that molecules have a real size, this contribution is always present. Consequently the latter (together with other forms of solute – solute repulsions) contribute to cases where $\gamma_j > 1.0$, $\ln(\gamma_j) > 0$ and $\mu_j(\ \mathrm{aq;\ real;\ T;p}) > \mu_j(\mathrm{aq;\ ideal\ ;T;p})$. In principle, activity coefficient γ_j contains an enormous amount of information [4]. Many of the interesting properties of aqueous solutions are packed in the parameter γ_j. Unfortunately only in rare instances is it possible to dissect a given γ_j into the several contributing interactions. A common though obviously dangerous procedure sets γ_j equal to unity, assuming that the properties of a given solute j are ideal. However in many cases we have no alternative but to make this assumption at least in initial stages of an analysis of experimental results.

Equation (e) is satisfactory for very dilute solutions of neutral solutes. Indeed this equation has enormous technological significance. The task of producing a very pure liquid requires lowering the molalities of solutes in a solution. With decreasing molality of a given solute, the chemical potential of a solute decreases; i.e. the solute is stabilised. So as more solute, an impurity, is removed, the trace remaining is increasingly stabilised [5].

We cannot put a number value to either $\mu_j(\mathrm{aq;T;p})$ or $\mu_j^0(\mathrm{aq;T})$. These quantities measure the contribution made by a solute j to the total energy of a solution. One contribution to, for example, $\mu_j^0(\mathrm{aq;T})$ emerges from solvent-solute interactions. Interestingly, we can in general put a number value to the corresponding limiting partial molar volume, $V_j^{\infty}(aq)$ [6]. The concept of infinite dilution is extremely important in a practical sense. Nevertheless, we enter a word of caution. Returning to equation (b) for the chemical potential, we note that $\mathrm{limit}\ (\mathrm{m_j} \to 0) \ln(\mathrm{m_j})$ tends to minus ∞.

$$\mathrm{Hence\ (at\ all\ T\ and\ p)\ limit}\ \ (\mathrm{m_j} \to 0)\, \mu_j(\mathrm{aq}) = -\infty$$

The practical significance of equation (i) is that with increasing dilution so the chemical potential of a solute decreases - the solute is increasingly stabilised. That is why the challenge of removing the last traces of unwanted solute presents such a formidable task, particularly to those industries where very high solvent purity is essential; e.g. the pharmaceutical industry [5].

Footnotes

[1] Activity coefficients have a ‘bad press’. They are not ‘loved’ except by a minority of chemists. Nevertheless these coefficients contain information concerning the way in which solute molecules ‘communicate’ to each other in solution.

[2] M. Spiro, Educ. Chem.,1966, **3**,139.

[3] The concept of an activity coefficient for a solute tending to unity at infinite dilution was proposed by A.A. Noyes and W.C. Bray: J. Am. Chem. Soc., 1911, **33**,1643.

[4] E. Wilhelm, Thermochim. Acta, 1987,119,17; Interactions in Ionic and Non-Ionic Hydrates, ed. H. Kleenberg, Springer – Verlag, Berlin, 1987,p.118.

[5] S. F. Sciamanna and J. M. Prausnitz, AIChE J., 1987, **33**, 1315.

[6] Throughout this subject, it is good practice to examine equations describing the dependence of partial molar properties of solvent and solute in the limit that the composition of the solution tends to increasingly dilute solutions; see J. E. Garrod and T. M. Herringon, J. Chem. Educ., 1969, **46**, 165.

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1.5.13: Chemical Potentials- Solutes- Mole Fraction Scale

For the most part we use either the molality scale or the concentration scale to express the composition of aqueous solutions. Nevertheless, the mole fraction scale is often used. Hence we express the chemical potential of solute j, μ_j as a function of mole fraction of solute j, $\mathrm{x}_j\,[=\mathrm{n_j}/\left(\mathrm{n_1}+\mathrm{n_j}\right)]$. Note that we are relating the property $\mu_\mathrm{j}(\mathrm{aq};\mathrm{T};\mathrm{p})$ to the composition of the solution using a different method from that used where the composition is expressed in terms of the molality or concentration of a solutes. By definition at fixed temperature and fixed pressure,

$$\mu_j(aq;T;p) = \mu_j^0(aq;T;x-\text{ scale }) + RT\,\ln\left(x_j\,f_j^*\right) + \int_{p^0}^{p} V_j^\infty(aq;T)\,dp$$

$$\text{By definition, }\ \mathrm{limit}\,(\mathrm{x_j}\to 0)\,\mathrm{f_j^*} = 1 \text{ at all T and p.}$$

f_j^* is the asymmetric solute activity coefficient on the mole fraction scale. The word '*asymmetric*', although rarely used, emphasises the difference between f_j^* and the rational activity coefficients.

For solutions at ambient pressure, the integral term in equation (a) is negligibly small. At pressure p and temperature T,

$$\mu_j(aq) = \mu_j^0(aq;x-\text{ scale }) + RT\,\ln\left(x_j\,f_j^*\right)$$

For an ideal solution, f_j^* is unity. The reference state for the solute is the solution where the mole fraction of solute-j is unity. This is clearly a hypothetical solution but we assume that the properties of the solute j in this solution can be obtained by extrapolating from the properties of solute-j at low mole fractions [1]. For an ideal solution at ambient pressure and temperature,

$$\mu_j(\mathrm{aq;id}) = \mu_\mathrm{j}^0(\mathrm{aq;x-\text{ scale }}) + \mathrm{R\,T\,ln\,(x_j)}$$

$$\text{or, } \mu_j(\mathrm{aq;id}) - \mu_\mathrm{j}^0(\mathrm{aq;x-\text{ scale }}) = \mathrm{R\,T\,ln\,(x_j)}$$

Because, $\mathrm{x_j} < 1.0, \quad \ln(\mathrm{x_j}) < 0$ Hence, $\mu_\mathrm{j}(\mathrm{aq;id}) < \mu_\mathrm{j}^0(\mathrm{aq;x-\text{ scale }})$. The solute is at a lower chemical potential than in the solution reference state [1].

Footnote

[1] The extrapolation defining the reference state as a solution wherein the mole fraction of **solute** is unity might seem strange. In fact such long extrapolations are common in chemical thermodynamics. For example at 0.1 MPa and 298.15 K, liquid water is the stable phase. At 0.1 MPa and 273.15 K both water(ℓ) and ice-1h are the stable phases. Nevertheless we know that, assuming water(g) is an ideal gas, the volume occupied by 0.018 kg of water(g) at 273 K and 0.1 MPa equals 22.4 dm^3. The fact that this involves a long extrapolation into a state where water vapour is not the stable phase does not detract from the usefulness of the concept.

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1.5.14: Chemical Potentials; Solute; Concentration Scale

Both molalities and mole fractions are based on the masses of solvent and solute in a solution. Hence neither the molality m_j nor mole fraction x_j of a non-reacting solute depend on temperature and pressure. In fact, when we differentiate the equations for $\mu_j(\mathrm{aq;T})$ with respect to pressure we take advantage of the fact that m_j and x_j do not depend on pressure. In addition, molalities and mole fractions are precise; there is no ambiguity concerning the amount of solvent and solute in the solution.

However, when we describe the meaning and significance of the activity coefficient γ_j and the meaning of the term '*infinite dilution*' we refer to the distance between solute molecules. In fact, in reviewing the properties of solutions, chemists are often more interested in the distance between solute molecules than in their masses. [The same can be said about the interest shown by humans in the behaviour of other human beings!] Therefore, chemists often use concentrations to express the composition of solutions.

The concentration of solute c_j describes the amount of chemical substance j in a given volume of solution; $\mathrm{c_j = n_j/V}$. The common method for expressing c_j uses the unit 'moldm' [1,2]. By definition [at temperature T and pressure $p\,(\cong p^0)$]

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq;\,c-scale}) + \mathrm{R\,T\,\ln\,(c_j\,y_j/c_r)}$$

$\mathrm{c_r}$ is the reference concentration, $1\ \mathrm{moldm^{-3}}$; c_j is expressed using the same unit; y_j is the activity coefficient for the solute j on the concentration scale.

$$\mathrm{By\ definition,}\quad \mathrm{lim\,it}\,(c_j \to 0)\,y_j = 1 \quad (\mathrm{at\ all}\ T\ \mathrm{and}\ p\ )$$

$\mu_\mathrm{j}^0(\mathrm{aq;\,c\ -\ scale}\ )$ is the chemical potential of solute j in an ideal $(\mathrm{y_j} = 1.0)$ aqueous solution (at the same T and p) where the concentration of solute $\mathrm{c_j} = 1.0\ \mathrm{moldm^{-3}}$

Footnotes

[1] Using the base SI units, concentration is given by the ratio (n_j/V) where V is expressed using the unit $\mathrm{m^3}$; n_j is the amount of chemical substance *j*, the unit being the mole. Nevertheless in the present context, general practice uses the reference concentration $1\ \mathrm{moldm^{-3}}$; c_j is expressed using the unit, $\mathrm{moldm^{-3}}$. This practice emerges from the fact that for dilute aqueous solutions at ambient T and p, unit concentration of solute, $1\ \mathrm{moldm^{-3}}$ is almost exactly unit molality, $1\ \mathrm{molkg^{-1}}$.

[2] For comments on standard states see E. M. Arnett and D. R. McKelvey, in Solute-Solvent Interactions, ed. J. F. Coetzee, M. Dekker, New York, 1969, chapter 6.

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1.5.15: Chemical Potentials- Solute- Concentration and Molality Scales

For a given solution we can express the chemical potential of solute j, $\mu_{\mathrm{j}}(\mathrm{aq})$ in an aqueous solution at temperature T and pressure $\mathrm{p}\,(\approx \mathrm{p}^0)$ using two equations. Therefore, at fixed T and p,

$$\mu_{\mathrm{j}}^0(\mathrm{aq}) + \mathrm{R\,T}\,\ln\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^0\right) = \\ \mu_{\mathrm{j}}^0(\mathrm{aq;c-\ scale\ }) + \mathrm{R\,T}\,\ln\left(\mathrm{c_j}\,\mathrm{y_j}/\mathrm{c_r}\right)$$

Therefore,

$$\ln\left(\mathrm{y_j}\right) = \ln\left(\gamma_{\mathrm{j}}\right) + \ln\left(\mathrm{m_j}\,\mathrm{c_r}/\mathrm{m}^0\,\mathrm{c_j}\right) + (1/\mathrm{R\,T})\ \left[\mu_{\mathrm{j}}^0(\mathrm{aq}) - \mu_{\mathrm{j}}^0(\mathrm{aq;c-\ scale\ })\right]$$

In the latter two equations the composition variables m_j and c_j are expressed in the units 'molkg^{-1}' and 'moldm^{-3}' respectively [1]. The ratio '$\mathrm{c_j}/\mathrm{m_j}$' equals the density expressed in the unit 'kgdm^{-3}'. For dilute solutions, $\mathrm{c_j}/\mathrm{m_j} = \rho_1^*(\ell)$, the density of the pure solvent.

$$\text{Also, } \mathrm{c_r}/\mathrm{m}^0 = \left[\mathrm{molddm}^{-3}\right] / \left[\mathrm{molkg}^{-1}\right] = \left[\mathrm{kgdm}^{-3}\right]$$

For dilute aqueous solutions at ambient pressure and $298.2\ \mathrm{K}$ [2,3],

$$\ln\left(\mathrm{m_j}\,\mathrm{c_r}/\mathrm{m}^0\,\mathrm{c_j}\right) = -\ln(0.997)$$

With reference to equation (b), with increasing dilution, $\mathrm{y_j} \to 1, \gamma_{\mathrm{j}} \to 1, (\ \mathrm{m_j}\,\mathrm{c_r}/\mathrm{m}^0\,\mathrm{c_j}) \to \mathrm{c_r}/\mathrm{m}^0\,\rho_1^*(\ell)$ Hence,

$$\mu_{\mathrm{j}}^0(\mathrm{aq;c-scale}) - \mu_{\mathrm{j}}^0(\mathrm{aq}) = \mathrm{R\,T}\,\ln\left[\mathrm{c_r}/\mathrm{m}^0\,\rho_1^*(\ell)\right]$$

We combine equations (b) and (e).

$$\ln\left(\mathrm{y_j}\right) = \ln\left(\gamma_{\mathrm{j}}\right) + \ln\left(\mathrm{m_j}\,\mathrm{c_r}/\mathrm{m}^0\,\mathrm{c_j}\right) - \ln\left[\mathrm{c_r}/\mathrm{m}^0\,\rho_1^*(\ell)\right]$$

$$\ln\left(\mathrm{y_j}\right) = \ln\left(\gamma_{\mathrm{j}}\right) + \ln\left(\mathrm{m_j}\,\mathrm{c_r}/\mathrm{m}^0\,\mathrm{c_j}\right) - \ln\left[\mathrm{c_r}/\mathrm{m}^0\,\rho_1^*(\ell)\right]$$

Footnotes

[1] A given solution is prepared by adding n_j moles of solute j to $\mathrm{w}_1\ \mathrm{kg}$ of solvent.

Molality of solute $\mathrm{j}/\mathrm{molkg}^{-1} = (\mathrm{n_j}/\mathrm{w}_1)$

Total mass of solution/kg $= w_1 + n_j\,M_j$ where molar mass of solute/kg $\mathrm{mol}^{-1} = \mathrm{M_j}$

Volume of solution/$\mathrm{m}^3 = \mathrm{V}$

Density of solution $\rho/\mathrm{kgm}^{-3} = \left[\frac{\mathrm{w}_1+\mathrm{n_j\,M_j}}{\mathrm{V}}\right]$

By convention chemists express the composition of solutions in terms of (i) concentration using the unit 'moldm^{-3}' and (ii) molality using the unit, 'molkg^{-1}'. These composition scales stem from the fact that at $298.15\ \mathrm{K}$, $1\ \mathrm{dm}^3$ of water has a mass of approx. $1\ \mathrm{kg}$. So as we swap composition scales a conversion factor is often required .

For dilute solutions $w_1 > n_j\,M_j$ and density of solution ρ equals the density of the pure solvent (at same temperature and pressure), i.e. density $\rho = \rho 1(\ell)\mathrm{kgmm}^{-3}$

[2] A typical conversion takes the following form for water at $298.2\ \mathrm{K}$ and ambient pressure.

$$\begin{aligned}\text{Density } &= 0.997\ \mathrm{g\ cm}^{-3} = 0.997\left(10^{-3}\ \mathrm{kg}\right)\left(10^{-2}\ \mathrm{m}^{-3}\right) \\ &= 0.997\mathrm{X}10^3\ \mathrm{kg\ m}^{-3} \\ &= 997\ \mathrm{kg\ m}^{-3} = 0.997\ \mathrm{kgdm}^{-3}\end{aligned}$$

$$\text{Then } \frac{\mathrm{c_j}/\mathrm{moldm}^{-3}}{\mathrm{m_j}/\mathrm{molkg}^{-1}} = \frac{\mathrm{n_j}/\mathrm{mol}}{\mathrm{V}/\mathrm{dm}^3}\,\frac{\mathrm{w}_1/\mathrm{kg}}{\mathrm{n_j}/\mathrm{mol}} = \frac{\mathrm{w}_1/\mathrm{kg}}{\mathrm{V}/\mathrm{dm}^3} = \rho/\mathrm{kgdm}^{-3}$$

[3] $$\begin{aligned}\ln\left(\mathrm{m_j}\,\mathrm{c_r}/\mathrm{m}^0\,\mathrm{c_j}\right) &= \ln\left[\left(\mathrm{c_r}/\mathrm{m}^0\right)/\left(\mathrm{c_j}/\mathrm{m_j}\right)\right] \\ &= \ln\left[\left(\mathrm{kgdm}^{-3}\right)/\rho\right] = -\ln\left(\rho/\mathrm{kgddm}^{-3}\right)\end{aligned}$$

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1.5.16: Chemical Potentials- Solute- Molality and Mole Fraction Scales

The chemical potential of solute j in aqueous solution at temperature T and at close to ambient pressure is related to the molality m_j and mole fraction x_j [1].

$$\mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_{\mathrm{j}}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right) = \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p};\mathrm{x}-\mathrm{scale}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{x}_{\mathrm{j}}\,\mathrm{f}_{\mathrm{j}}^{*}\right)$$

Therefore,

$$\ln\left(\mathrm{f}_{\mathrm{j}}^{*}\right) = \ln\gamma_{\mathrm{j}} + \ln\left(\mathrm{m}_{\mathrm{j}}/\mathrm{x}_{\mathrm{j}}\,\mathrm{m}^{0}\right) + (\mathrm{l}/\mathrm{R}\,\mathrm{T})\left[\mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) - \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p};\mathrm{x}\text{ - scale }\right)]$$

For dilute solutions [1], $(1/\mathrm{M}_1) > \mathrm{m}_{\mathrm{j}}$. Hence $(\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\,\mathrm{x}_{\mathrm{j}})$ equals $(m^{0}\,M_1)^{-1}$, a dimension-less quantity. Therefore,

$$\ln\left(f_j^{*}\right) = \ln\gamma_j - \ln\left(m^{0}\,M_1\right) + (1/RT)\left[\mu_j^{0}(aq;T;p) - \mu_j^{0}(aq;T;p;x-scale)\right]$$

It is unrealistic to expect that $\mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p})$ equals $\mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p};\mathrm{x}-\mathrm{scale})$ because the two reference states for solute-j are quite different. In general terms, $\mathrm{f}_{\mathrm{j}}^{*}$ does not equal γ_j for the same solution. Nevertheless, both $\mathrm{f}_{\mathrm{j}}^{*}$ and γ_j tend to the same limit, unity, as the solution approaches infinite dilution.

Hence as n_j tends to zero,

$$\mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) - \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p};\mathrm{x}-\mathrm{scale}) = \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}^{0}\,\mathrm{M}_1\right)$$

For example, in the case of aqueous solutions at 298.15 K, $\mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}^{0}\,\mathrm{M}_1\right)$ equals $\left(-9.96\ \mathrm{kJ\ mol}^{-1}\right)$ meaning that, with respect to the reference states for the two solutions, the chemical potential of solute j is higher on the mole fraction scale than on the molality scale. Combination of equations (b) and (d) yields an equation relating the two activity coefficients with the two terms describing the composition of the solution.

$$\ln\left(f_j^{*}\right) = \ln\gamma_j + \ln\left(m_j\,M_1/x_j\right)$$

The term 'unitary' is sometimes used to describe reference chemical potentials on the mole fraction scale, $\mu_{\mathrm{j}}^{0}\,(\mathrm{aq};\mathrm{T};\mathrm{p};\mathrm{x}_{\mathrm{j}}=1)$. The term $\mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}^{0}\,\mathrm{M}_1\right)$ in equation (d) is called cratic [2] because it refers to different amounts of solute and solvent which are **mixed** to form reference states for the solute on molality, mole fraction and concentration scales. The impression is sometimes given that standard states for solutes based on the mole fraction scale (sometimes identified as the unitary scale) are more fundamental but there is little experimental evidence to support this view.

Footnotes

[1] For a solution prepared using w_1 kg of water and n moles of solute j,

$$\mathrm{x}_{\mathrm{j}} = \mathrm{n}_{\mathrm{j}}/\left[(\mathrm{w}_1/\mathrm{M}_1) + \mathrm{n}_{\mathrm{j}}\right] \text{ and } \mathrm{m}_{\mathrm{j}} = \mathrm{n}_{\mathrm{j}}/\mathrm{w}_1$$
$$\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\,\mathrm{x}_{\mathrm{j}} = \mathrm{n}_{\mathrm{j}}\left[(\mathrm{w}_1/\mathrm{M}_1) + \mathrm{n}_{\mathrm{j}}\right]/\mathrm{w}_1\,\mathrm{m}^{0}\,\mathrm{n}_{\mathrm{j}}$$
$$\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\,\mathrm{x}_{\mathrm{j}} = \left[(1/\mathrm{M}_1) + \mathrm{m}_{\mathrm{j}}\right]/\mathrm{m}^{0}$$

[2] The terms '*unitary*' and '*cratic*' were suggested by R. W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.

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1.5.17: Chemical Potentials- Solutions- Salts

We consider a salt j having the following general formula;

$$v_+ \mathrm{M}^{z+} v_- \mathrm{X}^{z-}.$$

Here ν_+ and ν_- are the (integer) stoichiometric coefficients; z, and z_- are the (integer) charge numbers. We assume the salt j is completely dissociated in aqueous solution. Hence the solution contains (apart from solvent) two chemical substances. With complete dissociation each mole of salt produces $v (= v_+ + v_-)$ moles of ions. The condition of electric neutrality is expressed by equation (b).

$$|v_+ z_+| = |v_- z_-|$$

For a solution molality m_j, the molalities of cations and anions are $\nu_+ \mathrm{m}_j$ and $\nu_- \mathrm{m}_j$ respectively. If the chemical potentials of cations and anions are $\mu_+(\mathrm{aq})$ and $\mu_-(\mathrm{aq})$ respectively, the chemical potential of salt j in aqueous solution (at molality, m_j temperature T and ambient pressure) is given by equation (c).

$$\mu_j(aq) = v_+ \mu_+(aq) + v_- \mu_-(aq)$$

In an ideal solution (at the same T and ambient pressure) where the molality of the salt j is $1\ \mathrm{molkg}^{-1}$.

$$\mu_\mathrm{j}^0(\mathrm{aq}) = \mathrm{v}_+ \mu_+^0(\mathrm{aq}) + \mathrm{v}_- \mu_-^0(\mathrm{aq})$$

For each ionic substance i, the chemical potential (at the same T and p) is given by equation (e) where γ_i is the single ionic activity coefficient.

$$\mu_\mathrm{i}(\mathrm{aq}) = \mu_\mathrm{i}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_i}\,\gamma_\mathrm{i}/\mathrm{m}^0\right)$$

Hence for the salt with $\mathrm{m}_+ = v_+\,\mathrm{m_j}$ and $\mathrm{m}_- = v_-\,\mathrm{m_j}$.

$$\begin{aligned}\mu_\mathrm{j}(\mathrm{aq}) = &\left[\mathrm{v}_+\ \mu_+^0(\mathrm{aq}) + \mathrm{v}_- - \mu_-^0(\mathrm{aq})\right] \\ &+ \mathrm{v}_+\,\mathrm{R\,T\ ln}\left(\mathrm{v}_+\,\mathrm{m_j}\,\gamma_+/\mathrm{m}^0\right) \\ &+ \mathrm{v}_-\,\mathrm{R\,T\ ln}\left(\mathrm{v}_-\,\mathrm{m_j}\,\gamma_-/\mathrm{m}^0\right)\end{aligned}$$

We draw together the logarithm terms.

$$\begin{aligned}\mu_j(\mathrm{aq}) = &\left[v_+\ \mu_+^0(\mathrm{aq}) + \mathrm{v}_-\,\mu_-^0(\mathrm{aq})\right] \\ &+ \mathrm{R\,T\ ln}\left[\left(\mathrm{v}_+\,\mathrm{m_j}\,\gamma_+/\mathrm{m}^0\right)^{\mathrm{v}+}\ \left(\mathrm{v}_-\,\mathrm{m_j}\,\gamma_-/\mathrm{m}^0\right)^{\mathrm{v}-}\right]\end{aligned}$$

The latter far from elegant equation contains all the parameters we expect to be present. Here it is convenient to introduce a parameter Q [1,3].

$$\mathrm{Q}^v = v_+^{v+}\, v_-^{v-}$$

The (geometric) mean activity coefficient is defined by equation (i).

$$\gamma_\pm^v = \gamma_+^{v+}\,\gamma_-^{v-}$$

Hence equation (g) can be rewritten in the following form.

$$\mu_j(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + v\,\mathrm{R\,T\ ln}\left[\mathrm{Q\,m_j}\,\gamma_\pm/\mathrm{m}^0\right]$$

The quantity Q takes account of the stoichiometric composition of the salt. In preparing the salt solution we target the molality but this does not take account of how many moles of each ionic substance are produced by one mole of salt; the quantity ν only records how many moles of ionic substances are produced by each mole of salt. For the salt $\mathrm{M}^{2+}2\mathrm{X}^-$ [e.g. \mathrm{Mg Br}_{2}\)] $v_+ = 1$, $v_- = 2$ where $\mathrm{Q}^3 = 1^2.\ 2^2 = 4$. For this salt,

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + 3\,\mathrm{R\,T\ ln}\left[4^{1/3}\,\mathrm{m_j}\,\gamma_\pm/\mathrm{m}^0\right]$$

The complex algebra associated with a thermodynamic description of salt solutions stems from a conflict of interests and practical chemistry. The ground rules in this subject are quite simple--- measurements are made on electrically neutral solutions; e.g.

$\mathrm{NaCl(aq)}$. In the latter case chemists often favour a description of this system in terms of an aqueous solution of two solutes, sodium ions and chloride ions. Rather than using an activity coefficient for the solute [e.g; $\gamma(\mathrm{NaCl})$], we define a mean activity coefficient $\gamma_{\pm}$ which recognises the presence of two ionic substances. An indication of the presence of two solutes (i.e. $\mathrm{Na^+}$ and $\mathrm{Cl^-}$) rather than one solute (e.g. \mathrm{NaCl}\)) is the stoichiometric parameter ν in the equation for the chemical potential of the solvent. This parameter is readily determined from the depression of solvent freezing points (i.e. cryoscopy) and osmotic pressures. Both properties are directed at the properties of solvents. The cryoscopic technique is based on measurement of the temperature at which solvent in a solution is in equilibrium (at fixed pressure) with pure solid solvent. The osmotic pressure π characterises the equilibrium (a fixed temperature) between the solution at pressure $\mathrm{p}+\pi$ and pure solvent at pressure p. Both techniques determine ν or, in colloquial terms, count solute particles. The molar mass of NaCl and urea are roughly equal; the number of solute particles in $\mathrm{NaCl(aq)}$ is twice that in urea(aq) for the same mass of solute in $1\ \mathrm{kg}$ of water. We confirm this observation by measuring the depressions of freezing points or the osmotic pressures of two solutions.

Equation (j) signals an important challenge. If we could separate out ionic contributions to $\mu_{\mathrm{j}}^{0}(\mathrm{aq})$ for salt j, we could probe the contributions made by ion-water interactions, the hydration properties for a given ion i at defined T and p to $\mu_{j}^{0}(\mathrm{aq})$. In this exercise we might then extend the analysis to single ion enthalpies, $\mathrm{H_i^0(aq)}$, volumes $\mathrm{V_i^0(aq)}$, and entropies $\mathrm{S_i^0(aq)}$. Unfortunately the story is not simple. Indeed we cannot measure these chemical potentials and then obtain absolute estimates for the above derived properties.

Footnotes

[1] R. H. Stokes and R. H. Robinson, J. Am. Chem.Soc.,1948,**70**,1870.

[2] R. G. Bates, Pure Appl. Chem.,1973,**36**,407.

[3] J. C. R. Reis, J. Chem. Soc. Faraday Trans.,1997,**93**,2171.

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1.5.18: Chemical Potentials- Solutions- 1-1 Salts

There is an important point to consider in the context of salt solutions. For a dilute aqueous solution containing sodium chloride, osmotic and colligative properties confirm that for each mole of sodium chloride the aqueous solution contains (almost exactly) two moles of solutes. These observations result in an added complexity in that chemists describe the solute, sodium chloride in two ways. In one description there is one solute - 'sodium chloride'. In another description there are two solutes sodium ions and chloride ions. The latter description is certainly attractive because we can ring the changes through a series of solutes; $\mathrm{NaCl} \rightarrow \mathrm{NaBr} \rightarrow \mathrm{KBr} \rightarrow \mathrm{KCl} \rightarrow$ etc. Here we change in stepwise fashion one chemical substance in the salt to produce a new solute. There is, however, one crucial condition. Aqueous solutions are electrically neutral although the solutions contain ions. Therefore, the total charge on all cations equals in magnitude the total charge on all anions in the same solution. There is, therefore, a major problem. We cannot examine the properties of aqueous solutions containing, for example, just cations. We can only examine the properties of electrically neutral solutions. How can we obtain the properties of ionic substance (e.g. Na^{+}) in aqueous solutions at defined temperature and pressure? The frustrating answer is that we cannot measure the thermodynamic properties of single ions in solution. This realisation does not stop us speculating about such properties. In fact, a common procedure involves estimating the properties of single ions but then in the last stage of the analysis we pull the derived single ion properties together to describe the properties of a given salt solution.

The chemical potential of each ionic substance i in solution is related to its molality mi using equation (a) for a solution at fixed temperature and fixed pressure. We assume that the latter is ambient pressure and therefore close to the standard pressure p^{0}.

$$\mu_i(aq) = \mu_i^0(aq) + RT\,\ln\left(m_i\,\gamma_i/m^0\right)$$

Here $\mu_{\mathrm{i}}^{0}(\mathrm{aq})$ is the standard chemical potential of ion i in an aqueous solution where both the molality $\mathrm{m_i}$ and single ion activity coefficient \(\gamma_{\mathrm{i}}\) are unity (at the same T and p). However, the terms $\mu_i(\mathrm{aq})$, $\mu_{\mathrm{i}}^{0}(\mathrm{aq})$ and γ_{i} have no practical significance because, we cannot prepare a solution containing just one ionic chemical substance. The way forward involves using equation (a) for all ionic substances in the solution. In order to show how the argument develops we consider an aqueous solution containing a 1:1 salt (e.g. NaCl) which we assert is fully dissociated into ions. We make two (extrathermodynamic) assumptions.

i.

ii. The chemical potential of salt j in an ideal solution at unit salt molality ($\mathrm{m}_j = 1.0\ \mathrm{molkg}^{-1}$) is given by the sum of the corresponding reference chemical potentials of cations and anions (at the same temperature and pressure).

$$\mu_j\left(\mathrm{aq;id;m_j} = 1\ \mathrm{mol\ kg}^{-1}\right) =$$
$$\mu_+\left(\mathrm{aq;id;m_+} = 1\ \mathrm{mol\ kg}^{-1}\right) + \mu_-\left(\mathrm{aq;id;m_-} = 1\ \mathrm{mol\ kg}^{-1}\right)$$

As demanded by the analysis, such an ideal solution would be electrically neutral. But we have no information concerning the contributions which the ions make to the overall chemical potential, $\mu_{\mathrm{j}}\left(\mathrm{aq;id;m_j} = 1\ \mathrm{molkg}^{-1}\right)$. We anticipate that such contributions are characteristic of the ions. For a 1:1 salt combination of the three previous equations yields for a solution at fixed T and p, equation (d).

$$\mu_j(\mathrm{aq}) =$$
$$\mu_j^0\left(\mathrm{aq;id;m_j} = 1\ \mathrm{mol\ kg\ kg}^{-1}\right) + \mathrm{R\,T\,ln}\left(\mathrm{m_+\,m_-}\,\gamma_+\,\gamma_-/\mathrm{m}^0\,\mathrm{m}^0\right)$$

A (geometric) mean ionic activity coefficient $\gamma_{\pm}$ is defined by equation (e).

$$\gamma_{\pm}^2 = \gamma_+\,\gamma_-$$

Also for a 1: 1 salt $\mathrm{m_j^2} = \mathrm{m_+\ m_-}$. Therefore (at fixed temperature and pressure),

$$\mu_j(aq) = \mu_j^0(aq) + 2\,RT\,\ln\left(m_j\,\gamma_{\pm}/m^0\right)$$

where $\mu_j^0(\mathrm{aq}) = \mu_{\mathrm{j}}^{0}\left(\mathrm{aq;id;m_j} = 1\ \mathrm{mol\ kg}^{-1}; \mathrm{p} \equiv \mathrm{p}^0\right)$

$$\text{By definition limit}\ \ (\mathrm{m_j} \rightarrow 0)\ \gamma_{\pm} = 1.0\ \text{at all T and p}$$

The origin of the integer '2' in equation (f) is the stoichiometry of the salt; each mole of salt forms **two** moles of ions assuming complete dissociation. Hence $\mu_{\mathrm{j}}^{0}(\mathrm{aq})$ ( ) is the chemical potential of salt j in an ideal solution at the same T and $\mathrm{p\_}$ ($\cong \mathrm{p}^0$) where the

molality of the salt is $1\ \mathrm{molkg^{-1}}$. If the properties of the salt are ideal the chemical potential of the salt is given by equation (h).

$$\mu_j(\mathrm{aq;id}) = \mu_\mathrm{j}^0(\mathrm{aq}) + 2\,\mathrm{R\,T\,\ln\left(m_j/m^0\right)}$$

When $\mathrm{m_j} > \mathrm{m^0}$, the chemical potential of the salt in the ideal solution $\mu_j(\mathrm{aq;id}) > \mu_\mathrm{j}^0(\mathrm{aq})$; the salt is at a higher chemical potential than in the reference state. When $\mathrm{m_j} < 1.0\ \mathrm{molkg^{-1}}$, the chemical potential of the salt in the ideal solution is lower than in the reference solution where $\mathrm{m_j} = 1.0\ \mathrm{mol\ kg^{-1}}$.

Returning to the equation (f), there is merit in writing the equation in the following form.

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + 2\,\mathrm{R\,T\,\ln\left(m_j/m^0\right)} + 2\,\mathrm{R\,T\,\ln\left(\gamma_\pm\right)}$$

$$\mathrm{Or,}\quad \mu_j(\mathrm{aq}) = \mu_j(\mathrm{aq;id}) + 2\,\mathrm{R\,T\,\ln\left(\gamma_\pm\right)}$$

The difference $[\mu_j(\mathrm{aq}) - \mu_\mathrm{j}(\mathrm{aq;id})]$ is a measure of the extent to which the chemical potential of a salt in a real salt solution differs from the chemical potential of the same salt in an ideal solution. For $\mathrm{KCl(aq;\ 298.2\ K;\ 0.1\ molkg^{-1}})$ the mean ionic activity coefficient $\gamma_\pm$ equals 0.769; $0.769; 2\ \mathrm{R\ T\ ln}(0.769) = -1.30\ \mathrm{kJ\ mol^{-1}}$. In other words, KCl in this solution is at a lower chemical potential than in the corresponding ideal solution. In fact, $\gamma_\pm$ for most dilute aqueous salt solution is < 1.0 at ambient T and p, and so this pattern in chemical potentials is quite common. However, even though we know $\gamma_\pm$ for these systems we are not in a position to comment on the single ion activity coefficients for the reasons discussed above [1].

The difference described by equation (j) prompts the definition of an excess chemical potential, $\mu_\mathrm{j}^\mathrm{E}(\mathrm{aq})$.

$$\mathrm{Thus}\quad \mu_\mathrm{j}^\mathrm{E}(\mathrm{aq}) = 2\,\mathrm{R\,T\,\ln\left(\gamma_\pm\right)}$$

A key contribution to $\mu_j^0(\mathrm{aq})$ emerges from cation-water and anion-water interactions, namely ionic hydration. In contrast $\gamma_\pm$ is determined by ion-ion interactions in real solutions. For a solution at pressure p, equation (f) takes the following form.

$$\mu_\mathrm{j}(\mathrm{aq;p}) = \mu_\mathrm{j}^0\left(\mathrm{aq;p^0}\right) + 2\,\mathrm{R\,T\,\ln\left(m_j\,\gamma_\pm/m^0\right)} + \int_{\mathrm{p^0}}^{\mathrm{p}} \mathrm{V_j^\infty(aq)\,dp}$$

Footnotes

[1] For comparison of $\gamma_\pm$ for dilute salt solutions in aqueous solution and in $\mathrm{D_2O}$ see O. D. Bonner, J. Chem. Thermodyn., 1971, **3**,837; and references therein.

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1.5.19: Chemical Potentials- Solutions- Salt Hydrates in Aqueous Solution

An aqueous solution is prepared using n_j moles of salt MX and n_1 moles of water. The properties of the system are accounted for using one of two possible Descriptions.

Description I

The solute j comprises a 1:1 salt MX molality Missing \left or extra \right.

The single ion chemical potentials, are defined in the following manner

$$\mu\left(\mathrm{M}^{+}\right)=\left[\partial \mathrm{G} / \partial \mathrm{n}\left(\mathrm{M}^{+}\right)\right]_{\mathrm{T,p,n_1,n(x^-)}}$$
$$\mu\left(\mathrm{X}^{-}\right)=\left[\partial \mathrm{G} / \partial \mathrm{n}\left(\mathrm{X}^{-}\right)\right]_{\mathrm{T,p,n_1,n(M^+)}}$$

The total Gibbs energy (at fixed T and p where $p \approx p^0$) is given by equation (b).

$$\begin{aligned}\mathrm{G}(\mathrm{aq} ; \mathrm{I}) &= \mathrm{n}_1 \mu_1^{\mathrm{eq}}(\mathrm{aq}) \\ &+\mathrm{n}_\mathrm{j}\left\{\mu^0\left(\mathrm{M}^{+} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left[\mathrm{m}\left(\mathrm{M}^{+}\right)\,\gamma_{+}(\mathrm{I}) / \mathrm{m}^0\right]\right\} \\ &+\mathrm{n}_\mathrm{j}\left\{\mu^0\left(\mathrm{X}^{-} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left[\mathrm{m}\left(\mathrm{X}^{-}\right)\,\gamma_{-}(\mathrm{I}) / \mathrm{m}^0\right]\right\}\end{aligned}$$

Description II

According to this Description each mole of cations is hydrated by \(\mathrm{h}_{\mathrm{m}}\left(\mathrm{H}_2\mathrm{O}\right)\) moles of water and each mole of anions is hydrated by \(\mathrm{h}_{\mathrm{x}}\left(\mathrm{H}_2\mathrm{O}\right)\) moles of water.

The single ion chemical potentials are defined as follows.

$$\mu\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O}\right)=\left[\partial \mathrm{G} / \partial\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O}\right)\right]$$

at constant T, p, $\mathrm{n}\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O}\right),\left[\mathrm{n}_1-\mathrm{n}_\mathrm{j}\,\left(\mathrm{h}_{\mathrm{m}}+\mathrm{h}_{\mathrm{x}}\right)\right]\left(\mathrm{H}_2\mathrm{O}\right) \mu\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O}\right)=\left[\partial \mathrm{G} / \partial \mathrm{n}\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O}\right)\right]$

$$\text{at constant } \mathrm{T}, \mathrm{p}, \mathrm{n}\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O}\right),\left[\mathrm{n}_1-\mathrm{n}_\mathrm{j}\,\left(\mathrm{h}_{\mathrm{m}}+\mathrm{h}_{\mathrm{x}}\right)\right]\left(\mathrm{H}_2\mathrm{O}\right)$$

$$\mathrm{m}\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O}\right)=\mathrm{n}_\mathrm{j} / \mathrm{M}_1\,\left[\mathrm{n}_1-\left(\mathrm{h}_{\mathrm{m}}+\mathrm{h}_{\mathrm{x}}\right)\,\mathrm{n}_\mathrm{j}\right];$$

$$\mathrm{m}\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O}\right)=\mathrm{n}_\mathrm{j} / \mathrm{M}_1\,\left[\mathrm{n}_1-\left(\mathrm{h}_{\mathrm{m}}+\mathrm{h}_{\mathrm{x}}\right)\,\mathrm{n}_\mathrm{j}\right].$$

The (equilibrium) Gibbs energy (at defined T and p) is given by the following equation.

$$\begin{aligned}&\mathrm{G}(\mathrm{aq} ; \mathrm{II})=\left[\mathrm{n}_1-\mathrm{n}_\mathrm{j}\,\left(\mathrm{h}_{\mathrm{m}}+\mathrm{h}_{\mathrm{x}}\right)\right]\,\mu_1(\mathrm{aq}) \\ &+\mathrm{n}_\mathrm{j}\,\left[\mu^0\,\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O}\right)\,\gamma_{+}(\mathrm{II}) / \mathrm{m}^0\right\}\right] \\ &+\mathrm{n}_\mathrm{j}\,\left[\mu^0\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O}\right)\,\gamma_{-}(\mathrm{II}) / \mathrm{m}^0\right\}\right]\end{aligned}$$

But the Gibbs energies defined by equations (b) and (g) are identical (at equilibrium at defined T and p). After all, it is the same solution. Hence, (dividing by n_j)

$$\begin{aligned}&\left[\mu^0\left(\mathrm{M}^{+} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{M}^{+} ; \mathrm{I}\right)\,\gamma_{+}(\mathrm{I}) / \mathrm{m}^0\right\}\right] \\ &\quad+\left[\mu^0\left(\mathrm{X}^{-} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{X}^{-} ; \mathrm{I}\right)\,\gamma_{-}(\mathrm{I}) / \mathrm{m}^0\right\}\right]= \\ &\quad-\left(\mathrm{h}_{\mathrm{m}}+\mathrm{h}_{\mathrm{x}}\right)\,\mu_1^{\mathrm{eq}}(\mathrm{aq})+ \\ &\quad\left[\mu^0\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O}\right)\,\gamma_{+}(\mathrm{II}) / \mathrm{m}^0\right\}\right] \\ &+\left[\mu^0\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O}\right)\,\gamma_{-}(\mathrm{II}) / \mathrm{m}^0\right\}\right] \\ &\text{Then, } \mu^0\left(\mathrm{M}^{+} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{M}^{+} ; \mathrm{I}\right)\,\gamma_{+}(\mathrm{I}) / \mathrm{m}^0\right\} \\ &+\mu^0\left(\mathrm{X}^{-} ; \mathrm{aq}^0\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}(\mathrm{X} ; \mathrm{I})\,\gamma_{-}(\mathrm{I}) / \mathrm{m}^0\right\} \\ &=-\left(\mathrm{h}_{\mathrm{m}}+\mathrm{h}_{\mathrm{x}}\right)\,\left\{\mu_1^*(\ell)-2\,\phi\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m}_\mathrm{j}\right\} \\ &+\left\{\mu^0\left(\mathrm{M}^{+}\,\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{M}^{+}\mathrm{h}_{\mathrm{m}}\mathrm{H}_2\mathrm{O} ; \mathrm{II}\right)\,\gamma_{+}(\mathrm{II}) / \mathrm{m}^0\right\}\right] \\ &+\left[\mu^0\left(\mathrm{X}^{-}\,\mathrm{h}_{\mathrm{x}}\mathrm{H}_2\mathrm{O} ; \mathrm{aq}\right)+\mathrm{R}\,\mathrm{T}\,\ln\left\{\mathrm{m}\left(\mathrm{X}^{-}\mathrm{h}_{\mathrm{X}}\mathrm{H}_2\mathrm{O} ; \mathrm{II}\right)\,\gamma_{-}(\mathrm{II}) / \mathrm{m}^0\right\}\right]\end{aligned}$$

We use the latter equation to explore what happens in the limit that n_j approaches zero. Thus,

$$\text{limit}\,(n_j \to 0)\,\gamma_+(I) = 1 \quad \gamma_-(I) = 1$$
$$\gamma_+(II) = 1 \quad \gamma_-(II) = 1$$
$$m_j = 0$$
$$m\,(M^+ h_m H_2O; II)\; m\,(X^- h_x H_2O; II)\,/m\,(M^+; I)\; m\,(X^-; I) = 1.0$$

$$\text{Hence, } \mu^0\,(M^+; aq) + \mu^0\,(X^-; aq) =$$
$$\mu^0\,(M^+\, h_m H_2O; aq) + \mu^0\,(X^-\, h_x H_2O; aq)$$
$$-\,(h_m + h_x)\;\mu_1^*(\ell)$$

We obtain an equation linking the ionic chemical potentials. Thus,

$$\ln \gamma_+(I) + \ln \gamma_-(I) = 2\,\phi\,M_1\,m_j\;(h_m + h_x) + \ln\{\gamma_+(II)\} + \ln\{\gamma_-(II)\;\}$$

Missing \end{aligned}

We identify relationships between single ion activity coefficients in an extra-thermodynamic analysis. Thus from equation (l),

$$\ln\{\gamma_+(II)\;\} = \ln\{\gamma_+(I)\;\} - \phi\,M_1\,m_j\,h_m$$

$$\ln\{\gamma_-(II)\} = \ln\{\gamma_-(I)\} - \phi\,M_1\,m_j\,h_x$$

It is noteworthy that in these terms the solution can be ideal using description I where $\gamma_\pm = 1.0$ but non-ideal using description II. Nevertheless, these equations show how the activity coefficient of the hydrated ion (description II) is related to the activity coefficient of the simple ion (description I).

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1.5.20: Chemical Potentials- Salt Solutions- Ion-Ion Interactions

For most dilute aqueous salt solutions (at ambient temperature and pressure), mean ionic activity coefficients $\gamma_{\pm}$ are less than unity. Ion-ion interactions within a real solution lower chemical potentials below those of salts in the corresponding ideal solutions. A quantitative treatment of this stabilisation is enormously important. In fact for almost the whole of the 20th Century, scientists have offered theoretical bases for expressing $\ln(\gamma_{\pm})$ as a function of the composition of a salt solution, temperature, pressure and electrical permittivity of the solvent.

In effect we offer as much information as demanded by the theory (e.g. molality of salt, nature of salt, permittivity of solvent, ion sizes, temperature, pressure, ...). We set the apparently simple task - please calculate the mean activity coefficient of the salt in this solution.

Many models and treatments have been proposed [1]. Most models start by considering a reference j-ion in an aqueous salt solution. In order to calculate the electric potential at the j-ion arising from all other ions in solution, we need to know the distribution of these ions about the j-ion. Unfortunately this distribution is unknown and so we need a model for this distribution. Further activity coefficients also reflect the impact of ions on water-water interactions in aqueous salt solutions. [2]

Footnotes

[1]

a. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd. edition revised,1959.
b. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions ,Reinhold, New York,1950, 2nd. edn.,1950, chapter 2. The analysis presented by Harned and Owen anticipates application to irreversible processes; e.g. electrolytic conductance of salt solutions. We confine attention to equilibrium properties.

[2] H. S. Frank, Z. Phys. Chem, 1965,**228**,364.

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1.5.21: Chemical Potentials- Salt Solutions- Debye-Huckel Equation

The chemical potential of salt j in an aqueous solution at temperature T and pressure p (which is close to the standard pressure p^0) is related to the molality of salt m_j using equation (a).

$$\mu_j(aq) = \mu_j^0(aq) + v\,R\,T\,\ln\left(Q\,m_j\,\gamma_\pm/m^0\right)$$

$$\text{Here } Q^v = v_+^{v(+)}\,v_-^{v(-)}$$

In equation (b), ν_+ and ν_- are the number of moles of cations and anions respectively produced on complete dissociation by one mole of salt; $\nu = \nu_+ + \nu_-$. Here $\gamma_\pm$ is the mean ionic activity coefficient where by definition, at all T and p,

$$\text{limit}\,(m_j \to 0)\,\gamma_\pm = 1$$

If the thermodynamic properties of the solution are ideal than $\gamma_\pm$ is unity. However the thermodynamic properties of salt solutions, even quite dilute solutions, are not ideal as a consequence of strong long-range charge-charge interactions between ions in solution. The challenge is therefore to come up with an equation for $\gamma_\pm$ granted that the temperature, pressure and properties of the solvent and salt are known together with the composition of the solution. The first successful attempt to meet this challenge was published by Debye and Huckel in 1923 and 1924 [1,2].

In most published accounts, the CGS system of units is used. However here we use the SI system and trace the units through the treatment. The solvent is a dielectric (structureless) continuum characterised by its relative permittivity, ε_r. The solute (salt) comprises ions characterised by their charge and radius; e.g. for ion-*j*, charge $z_j\,e$ and radius r_j such that for cations $z_j \geq 1$ and for anions $z_j \leq -1$ where z_j is an integer.

The analysis combines two important physical chemical relationships; Boltzmann's Law and Poisson's Equation.

We consider an aqueous salt solution containing i-ionic substances, each substance having molality mi. The solution contains cations and anions. A KEY condition requires that the electric charge on the solution is zero.

$$\text{Thus, } \sum_{j=1}^{j=i} m_j\,z_j = 0$$

Published accounts of the Debye-Huckel equation almost always use the concentration scale because the analysis concentrates on the distances between ions in solution rather than their mass. The concentration of j ions in a solution, volume V, is given by equation (e)

$$\text{Thus, } \sum_{j=1}^{j=i} c_j\,z_j = 0$$

$$c_j = n_j/V$$

Here n_j is the amount of solute j (expressed using the unit, mole) and V is the volume of solution.

These equations describe the solution as seen from the standpoint of a chemist interested in the properties of a given solution. However the 'view' from the standpoint of, for example, a cation in the solution is quite different. The neutrality condition in equation (d) requires that the electric charge on the solution surrounding the cation j with charge $+|z_j\,e|$ equals $-|z_j\,e|$; i.e. equal in magnitude but opposite in sign. This is the electric charge on the rest of the solution and constitutes the 'ion atmosphere' of the j ion. Every ion in the solution has its own atmosphere having a charge equal in magnitude but opposite in sign. Moreover interaction between a j ion and its atmosphere stabilises the j ion in solution. The task of the theory is to obtain an equation for this stabilisation of the salt (i.e. the lowering of its chemical potential in solution). Intuitively we might conclude that this stabilisation is a function of the ionic strength of the salt solution and the dielectric properties of the solvent.

We consider a reference j ion, radius r_j, in solution together with a small volume element, dV, a distance not more than say ($50 \times r_j$) from the j ion. In terms of probabilities, if the j ion is a cation the probability of finding an anion in the reference volume is greater than finding a cation. Again with the j ion as reference, we identify a time averaged electric potential ψ_j at the volume element. The distribution of ions about the cation j is assumed to follow the Boltzmann distribution law. The time average number

of cations $\mathrm{dn_+}$ and anions $\mathrm{dn_-}$ in the volume element is given by equation (g) where ion i is, in turn, taken as a cation and then as an anion.

$$\mathrm{dn_i = p_i\ exp\left(-\frac{z_i\, e\, \psi_j}{k\, T}\right)\ dV}$$

Here $\mathrm{p_i}$ is the number of i ions in unit volume of the solution [3]. Each i ion has electric charge $z_i\, e$. Hence the electric charge on the volume dV is obtained by summing over the charge on the time average number of all ions. The charge density ρ_j is given by equation (h), where the subscript j on ρ_j stresses that the charge is described with respect to the charge on the j ion [4].

$$\mathrm{\rho_j = \sum p_i\, z_i\, e\ exp\left(-\frac{z_i\, e\, \psi_j}{k\, T}\right)}$$

The subscript j on ρ_j and ψ_j identifies the impact of ion j on the composition and electric potential of the reference volume dV distance r from the j ion. At this point some simplification is welcomed. We expand the exponential in equation (h) [5].

$$\text{Hence,}\quad \rho_j = \sum \mathrm{p_i\, z_i\, e} - \sum \mathrm{p_i\, z_i\, e}\left(\frac{\mathrm{z_i\, e\, \psi_j}}{\mathrm{k\, T}}\right) + \sum \mathrm{p_i\, z_i\, e\, (1/2)}\left(\frac{\mathrm{z_i\, e\, \psi_j}}{\mathrm{k\, T}}\right)^2 - \ldots\ldots$$

The solution as a whole has zero electric charge.

$$\text{Hence}\quad \sum \mathrm{p_i\, z_i\, e} = 0$$

$$\text{Also for dilute solutions,}\quad \left(\frac{\mathrm{z_i\, e\, \psi_j}}{\mathrm{k\, T}}\right) \ll < 1$$

Hence the third and all subsequent terms in equation (i) are negligibly small.

$$\text{Therefore } \rho_j = -\sum \frac{p_i\ (z_i\, e)^2\ \psi_j}{k\, T}$$

The approximation leading to equation (l) is welcome for an important reason. Equation (l) satisfies a key condition which requires a linear interdependence between ρ_j and ψ_j.

Equation (l) relates charge density ρ_j and electric potential ψ_j. These two properties are also related by Poisson's theorem [6]:

$$\nabla^2 \psi_j = -\rho_j / \varepsilon_0\, \varepsilon_\mathrm{r}$$

Here ε_0 is the permittivity of free space; \(\varepsilon_{\mathrm{r}}\) is the relative permittivity of the solvent [6]; ρ_j is the charge density per unit volume.

In the case considered here, the electric charges (ions) are spherically distributed about the reference j ion. Then Poisson's equation takes the following form [7].

$$\left[\frac{1}{r^2}\right]\ \frac{d}{dr}\left(r^2\ \frac{d\psi_j}{dr}\right) = -\frac{\rho_j}{\varepsilon_0\, \varepsilon_r}$$

Combination of equations (l) and (n) yields the key equation (o).

$$\left[\frac{1}{r^2}\right]\ \frac{d}{dr}\left(r^2\ \frac{d\psi_j}{dr}\right) = \frac{e^2}{\varepsilon_0\, \varepsilon_r\, k\, T} \sum p_i\, z_i^2\, \psi_j$$

$$\text{Or,}\quad \mathrm{\left[\frac{1}{r^2}\right]\ \frac{d}{dr}\left(r^2\ \frac{d\psi_j}{dr}\right) = \kappa^2\, \psi_j}$$

$$\text{where [8]}\kappa^2 = \frac{e^2}{\varepsilon_0\, \varepsilon_\mathrm{r}\, \mathrm{k\, T}} \sum \mathrm{p_i\, z_i^2}$$

Property κ has the unit 'reciprocal distance'. Equation (p) is a second order differential equation [9] having the general solution given by equation (p).

$$\psi_j = A_1\ \exp(-\kappa\, r)/r + A_2\ \exp(\kappa\, r)/r$$

However $\mathrm{limit}(r \to \infty) \exp(\kappa\, r)/r$ is very large where ψ_j is zero. Hence $\mathrm{A_2}$ must be zero.

$$\text{Therefore [10], } \Psi_j = \mathrm{A}_1 \exp(-\kappa \mathrm{r})/\mathrm{r}$$

We combine equations (l) and (s) [11].

$$\rho_j = -A_1 \frac{\exp(-\kappa\, r)}{r} \sum \frac{p_i\ (z_i\, e)^2}{k\, T}$$

Using the definition of κ^2 in equation (q) [12],

$$\rho_j = -A_1\, \varepsilon_0\, \varepsilon_\mathrm{r}\, \kappa^2\, \frac{\exp(-\kappa\, r)}{r}$$

At this point, a geometric condition is taken into account. Charge density ρ_j describes the electrical properties of the solution 'outside ' the j ion. No other ions can approach the j ion closer than a 'distance of closest approach' a_j. The total charge on the solution 'outside' the j ion equals in magnitude but opposite in sign that on the j ion. Hence,

$$4\,\pi \int_{a(j)}^{\infty} \rho_j\, r^2\, dr = -z_j\, e$$

$$\text{Or, } 4\,\pi \int_{a(j)}^{\infty} \left[-A_1\, \varepsilon_0\, \varepsilon_r\, K^2\, \frac{\exp(-K\, r)}{r}\right] r^2\, dr = -z_j\, e$$

This integration yields an equation for A_1.

$$A_1 = \frac{(z_j\, e)\ \exp{(\kappa\, a_j)}}{4\,\pi\, \varepsilon_0\, \varepsilon_\mathrm{r}\ (1 + \kappa\, a_j)}$$

$$\text{Hence } \psi_\mathrm{j} = \frac{(\mathrm{z_j\, e})\ \exp{(\kappa\, \mathrm{a_j})}}{4\,\pi\, \varepsilon_0\, \varepsilon_\mathrm{r}\ (1 + \kappa\, \mathrm{a_j})}\ \frac{\exp(-\kappa\, \mathrm{r})}{\mathrm{r}}$$

We recall that ψ_j is the electric potential at distance r from the j ion. In the event that the solution contains just the j ion (i.e. an isolated j ion) with charge $z_j\, e$, the electric potential $\psi(\text{ iso })$, distance r from the j ion, is given by equation (z) [13].

$$\psi_j(iS0) = \frac{z_j\, e}{4\,\pi\, \varepsilon_0\, \varepsilon_r\, r}$$

The electric potential psi_j given by equation (y) is the sum of $\psi(\text{ iso })$ and the electric potential produced by all other ions in solution $\psi(\text{ rest })$.

$$\text{Then} \quad \psi_j = \psi_j(\text{ iso }) + \psi_j(\text{ rest })$$

$$\text{Hence,} \quad \psi_\mathrm{j}(\text{ rest }) = \frac{\mathrm{z_j\, e}}{4\,\pi\, \varepsilon_0\, \varepsilon_\mathrm{r}\, \mathrm{r}} \left[\frac{\exp{(\kappa\, \mathrm{a_j})}\ \exp(-\kappa\, \mathrm{r})}{1 + \kappa\, \mathrm{a_j}} - 1\right]$$

Equation (zb) is valid for all values of r, including for $\mathrm{r} = \mathrm{a_j}$. Then from equation (zb), $\psi_\mathrm{j}(\text{ rest })$ at $\mathrm{r} = \mathrm{a_j}$ is given by equation (zc).

$$\psi_j(\text{ rest }) = -\frac{z_j\, e}{4\,\pi\, \varepsilon_0\, \varepsilon_r}\ \frac{\kappa}{1 + \kappa\, a_j}$$

We imagine that the j ion is isolated in solution and that the electrical interaction with all other i ions is then switched on at fixed T and p. The change in chemical potential of single j ion is given by equation (zd),

$$\Delta\mu_j(\mathrm{elec}) = -\frac{\mathrm{z_j^2\, e^2}}{4\,\pi\, \varepsilon_0\, \varepsilon_\mathrm{r}}\ \frac{\kappa}{1 + \kappa\, \mathrm{a_j}}$$

For one mole of j ions, $\Delta\mu_\mathrm{j}(\mathrm{elec})$ is given by equation (ze) where an additional factor of '2' is introduced into the denominator. Otherwise each ion would be counted twice; i.e. once as the j ion and once in solution around the j ion [14].

$$\Delta\mu_\mathrm{j}(\text{elec; one mole }) = -\frac{\mathrm{z_j^2\, e^2\, N_A}}{8\,\pi\, \varepsilon_0\, \varepsilon_\mathrm{r}}\ \frac{\kappa}{1 + \kappa\, \mathrm{a_j}}$$

The chemical potential of single ion j in an aqueous solution, $\mu_\mathrm{j}(\mathrm{aq})$ is related to molality m_j and single ion activity coefficient γ_j using equation (zf).

$$\mu_j(aq) = \mu_j^0(aq) + R\,T\,\ln\left(m_j/m^0\right) + R\,T\,\ln\left(\gamma_j\right)$$

Comparison of equations (ze) and (zf) yields equation (zg).

$$\ln\left(\gamma_j\right) = -\frac{z_j^2\,e^2}{8\,\pi\,\varepsilon_0\,\varepsilon_r\,k\,T}\,\frac{\kappa}{1+\kappa\,a_j}$$

The mean ionic activity coefficient $\gamma_\pm$ for the salt in solution is given by equation (zh); i.e. for a simple salt where each mole of salt contains ν_+ moles of cations and ν_- moles of anions.

$$\gamma_\pm = \left(\gamma_+^{v+}\,\gamma_-^{v-}\right)^{1/v}$$

$$\text{Or,}\quad (v_+ + v_-)\,\ln\left(\gamma_\pm\right) = v_+\,\ln\left(\gamma_+\right) + v_-\,\ln\left(\gamma_-\right)$$

We envisage closest approaches only between differently charged ions. Then for a given salt, $a_+ = a_- = a_j$. Hence from equation (zg),

$$\ln\left(\gamma_\pm\right) = -\frac{e^2}{8\,\pi\,\varepsilon_0\,\varepsilon_r\,k\,T}\left(\frac{\kappa}{1+\kappa\,a_j}\right)\left(\frac{v_+\,z_+^2 + v_-\,z_-^2}{v_+ + v_-}\right)$$

But the salt is overall electrically neutral.

$$\text{Or,}\quad V_+\,Z_+ = -V_-\,Z_-$$

$$\text{Whence,}\quad v_+ = -v_-\,z_-/z_+$$

$$\text{So [15],}\ \frac{v_+\,z_+^2 + v_-\,z_-^2}{v_+ + v_-} = -z_+\,z_-$$

Hence we arrive at an equation for the mean ionic activity coefficient, $\gamma_\pm$ [16].

$$\ln\left(\gamma_\pm\right) = \frac{z_+\,z_-\,e^2}{8\,\pi\,\varepsilon_0\,\varepsilon_s\,kT}\left(\frac{K}{1+\kappa\,a_j}\right)$$

At this point we return to equation (q) and recall that \(\mathrm{p}_{\mathrm{i}}\) is the number of ions in unit volume of solution. If the concentration of i ions equals c_i, (with N_A = the Avogadro constant),

$$\text{then [17]}\ p_i = N_A\,c_i$$

$$\text{Therefore [18]},\quad \kappa^2 = \frac{e^2\,(N_A)^2}{\varepsilon_0\,\varepsilon_r\,RT}\sum c_i\,z_i^2$$

The convention is to express concentrations using the unit, $\mathrm{mol dm^{-3}}$ for which we use the symbol, c'.

$$\text{Hence}\quad \kappa^2 = \frac{e^2\,(N_A)^2}{10^3\,\varepsilon_0\,\varepsilon_r\,R\,T}\sum c_i'\,z_i^2$$

For dilute solutions, the following approximation is valid where

$$\text{ionic strength}\ I = (1/2)\sum m_i\,z_i^2$$

$$\kappa^2 = \frac{2\,e^2\,(N_A)^2\,\rho_1^*(\ell)}{\varepsilon_0\,\varepsilon_r\,R\,T}\,I$$

From equations (zn) and (zs) [19],

$$\ln\left(\gamma_\pm\right) = \frac{z_+\,z_-\,e^2}{8\,\pi\,\varepsilon_0\,\varepsilon_r\,k\,T}\left[\frac{2\,e^2\,(N_A)^2\,\rho_1^*(\ell)}{\varepsilon_0\,\varepsilon_r\,R\,T}\right]^{1/2}\frac{(I)^{1/2}}{1+\kappa\,a_j}$$

For very dilute solutions, the Debye Huckel Limiting Law (DHLL) is used where it is assumed that $1 + \kappa\,a_j = 1.0$. Hence,

$$\ln\left(\gamma_\pm\right) = \frac{e^3\,[2\,N_A\,\rho_1^*(\ell)]^{1/2}}{8\,\pi\,\varepsilon_0\,\varepsilon_r\,k\,T}\left[\frac{N_A}{\varepsilon_0\,\varepsilon_r\,R\,T}\right]^{1/2} z_+\,z_-\,(I)^{1/2}$$

Equation (zu) may be written in the following form.

$$\ln(\gamma_{\pm}) = \frac{e^3\ [2\,N_A\,\rho_1^*(\ell)]^{1/2}}{8\,\pi\,\varepsilon_0\,\varepsilon_r\,k\,T}\left[\frac{N_A}{\varepsilon_0\,\varepsilon_r\,R\,T}\right]^{1/2} z_+\,z_-\,(I)^{1/2}$$

For aqueous solutions at ambient pressure and 298.15 K, $\rho_1^*(\ell) = 997.047\ \text{kg m}^{-3}$ and $\varepsilon_r = 78.36$.

$$\text{Hence [20]}\ \ \ln(\gamma_{\pm}) = (1.1749)\,z_+\,z_-\ \left(\text{I/molkg}^{-1}\right)^{1/2}$$

We note that with $Z_+\,Z_- = -\,|Z_+\,Z_-|$, $\ln(\gamma_{\pm}) < 0$.

In other words $\ln(\gamma_{\pm})$ is a linear function of the square root of the ionic strength I. Most authors choose to write equation (zx) using logarithms to base 10.

$$\text{Then}\ \ \log(\gamma_{\pm}) = |z_+\,z_-|\ A_\gamma\ \left(\text{I/molkg}^{-1}\right)^{1/2}$$

Here[22] $A_\gamma = 0.510$. Certainly the latter constant is readily remembered as 'one-half'. Slight disagreements between published estimates of A_γ are a result of different estimates of ε_r and $\rho_1^*(\ell)$. Harned and Owen [1d] published a useful Table for A_γ as a function of temperature for aqueous solutions.

The full equation for $\ln(\gamma_{\pm})$ following on from equation (zt) takes the following form [22].

$$\ln(\gamma_{\pm}) = \frac{-\,|z_+\,z_-|\ S_\gamma\ \left(\text{I/molkg}^{-1}\right)^{1/2}}{1 + \beta\,a_j\,(\text{I/molkg})^{-1})^{1/2}}$$

For aqueous solutions at ambient pressure and 298.15 K [5], $S_\gamma = 1.175$ and $\beta = 3.285\ \text{nm}^{-1}$. Adam [23] suggests that aj can be treated as a variable in fitting the measured dependence of $\ln(\gamma_{\pm})$ on ionic strength for a given salt.

Footnotes

[1] P. Debye and E. Huckel, Physik. Z.,1923, **24**,185,334;1924,**25**,97.

[2] For accounts of the theory see--

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h. R. J. Hunter, J.Chem.Educ.,1966,**43**,550.
i. For comments on the role of water-water and water-ion interactions in aqueous salt solutions see H. S. Frank, Z. fur physik. Chemie,1965,**228**,**364**.

[3] In equation (g), dni describes the **number** of ions in volume dV; p_i describes the number of ions in unit volume of solution. [In other words the units used to express p_i and dn_i differ.

$$\frac{z_i\,e\,\psi_j}{k\,T} = \frac{[1]\,[C]\,[V]}{[JK^{-1}]\,[K]} = \frac{[1]\,[As]\,[JA^{-1}\,s^{-1}]}{[JK^{-1}]\,[K]} = [1]$$

$$p_i\,\exp\left(-\frac{z_1\,e\,\psi_j}{k\,T}\right)\,dV = \left[\frac{1}{m^3}\right]\,[1]\,\left[m^3\right] = [1]$$

$$dn_i = [1] \quad p_i = \left[m^{-3}\right]$$

[4] $\frac{z_i\,e\,\psi}{k\,T} = \frac{[1]\,[C]\,[V]}{[JK^{-1}]\,[K]} = \frac{[As]\,[JA^{-1}\,s^{-1}]}{[J]} = [1]$ Then $\rho_j = \left[\frac{1}{m^3}\right]\,[1]\,[C] = \left[\frac{C}{m^3}\right]$; i.e. charge per unit volume

[5] $\exp(x) = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots\ldots$

$$\rho_j = \frac{[m^{-3}]\ [1]^2\,[C]^2\,[V]}{[JK^{-1}]\ [K]} = \frac{[m^{-3}]\ [As]^2\ [JA^{-1}\ s^{-1}]}{[J]} = [Cm^{-3}]$$

i.e. charge per unit volume

[6] $\nabla^2\psi_j = \frac{1}{[\,m^2]}\,[V] = \left[\frac{V}{m^2}\right]$

$$\rho_j/\varepsilon_0\,\varepsilon_r = \frac{[Cm^{-3}]}{[Fm^{-1}]\ [1]} = \frac{[Asm^{-3}]}{[AsV^{-1}m^{-1}]} = \left[\frac{V}{m^2}\right]$$

[7] $\left[\frac{1}{r^2}\right]\ \frac{d}{dr}\left(r^2\ \frac{d\psi_j}{dr}\right) = \left[\frac{1}{m^2}\right]\ \frac{1}{[m]}\ [m^2]\ \frac{[JA^{-1}\ s^{-1}]}{[m]} = \left[\frac{JA^{-1}\ s^{-1}}{m^2}\right]$

$$\frac{\rho}{\varepsilon_0\,\varepsilon_r} = \left[\frac{C}{m^3}\right]\ \frac{1}{[Fm^{-1}]}\ \frac{1}{[1]} = \left[\frac{As}{m^3}\right]\ \left[\frac{1}{AsV^{-1}\ m^{-1}}\right] = \left[\frac{V}{m^2}\right] = \left[\frac{JA^{-1}\ s^{-1}}{m^2}\right]$$

[8]

$$\kappa^2 = \frac{[C]^2}{[Fm^{-1}]\ [1]\ [JK^{-1}]\ [K]}\ \left[\frac{1}{m^3}\right]\ [1]^2$$
$$\kappa = [m^{-1}]$$

[9]

$$\frac{d}{dr}\left(r^2\,\frac{d\psi_j}{dr}\right) = 2\,r\,\frac{d\psi_j}{dr} + r^2\,\frac{d^2\psi_j}{dr^2} = \kappa^2\,\psi_j$$
$$\text{Then, } r^2\,\frac{d^2\psi_j}{dr} + 2\,r\,\frac{d\psi_j}{dr} - \kappa^2\,\psi_j = 0$$

[10] $\psi_j = [V]$ and $\psi_j = A_1\ \exp\left([m]^{-1}\,[m]\right)/[m] \quad A_1 = [Vm]$

[11] $\rho_j = \left[\frac{C}{m^3}\right]$

[12]

$$A_1\,\varepsilon_0\,\varepsilon_r\,\kappa^2\,\frac{\exp(-K\,r)}{r} = [Vm]\ \left[Fmm^{-1}\right]\ [1]\,[m]^{-2}\,\frac{[1]}{[m]}$$

[13] $\psi_j(\text{ iso }) = \frac{[1]\,[C]}{[1]\ [1]\ [Fm^{-1}]\ [1]\ [m]} = \frac{[As]}{[AsV^{-1}]} = [V]$

[14]

$$\Delta\mu_j(\text{elec; one mole }) = \frac{[1]^2\,[C]^2\,[mol]^{-1}}{[1]\ [Fm^{-1}]\ [1]}\ \left[\frac{[m]^{-1}}{1+[m]^{-1}\,[m]}\right]$$
$$= \frac{[As]^2\ \left[mol^{-1}\right]\ [m]^{-1}}{[\ A\ sV^{-1}\ m^{-1}]} = \frac{[As]\,[mol]^{-1}}{[\ J^{-1}\ A\ s]} = \left[Jmol^{-1}\right]$$

[15]

$$\frac{v_+\,z_+^2 + v_-\,z_-^2}{v_+ + v_-} = \frac{-\left(v_-\,z_-\,z_+\right) + \left(v_-\,z_-^2\right)}{-\left(v_-\,z_-/z_+\right) + v_-}$$
$$= -z_+\,z_-\left[\frac{v_- - \left(v_-\,z_-/z_+\right)}{-\left(v_-\,z_-/z_+\right) + v_-}\right] = -z_+\,z_-$$

[16]

$$\ln\left(\gamma_\pm\right) = \frac{[1]\,[C]^2}{[1]\ [Fm^{-1}]\ [1]\ [JK^{-1}]\ [K]}\ \left[\frac{[m]^{-1}}{1+[m]^{-1}\,[m]}\right]$$
$$= \frac{[As]^2}{[AsV^{-1}]}\ \frac{1}{[\ J]} = \frac{[As]}{[J^{-1}As]\ [J]} = [1]$$

[17] $N_A\,c_i = \left[mol^{-1}\right]\ \left[molm^{-3}\right] = \left[m^{-3}\right]$

[18]

$$\kappa^2 = \frac{[\mathrm{C}]^2\ \left[\mathrm{mol}^{-1}\right]^2}{[\ \mathrm{F\ m}^{-1}]\ [1]\ \left[\mathrm{Jmol}^{-1}\ \mathrm{K}^{-1}\right]\ [\mathrm{K}]}\ \left[\mathrm{molm}^{-3}\right]$$
$$= \frac{[\mathrm{As}]^2\,[\mathrm{m}]^{-2}}{[\ \mathrm{A\ sV}^{-1}]\ [\mathrm{J}]} = \frac{[\mathrm{As}]\,[\mathrm{m}]^{-2}}{\left[\ \mathrm{J}^{-1}\ \mathrm{A\ s}\right]\ [\mathrm{J}]} = [\mathrm{m}]^{-2}$$

[19]

$$\frac{\mathrm{z_+\,z_-\,e^2}}{8\,\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{k\,T}} = \frac{[1]\,[\mathrm{C}]^2}{[1]\,[1]\ \left[\mathrm{Fm}^{-1}\right]\ \left[\mathrm{JK}^{-1}\right]\ [\mathrm{K}]}$$
$$= \frac{\left[\mathrm{A}^2\ \mathrm{s}^2\right]}{\left[\mathrm{AsJ}^{-1}\mathrm{Asm}^{-1}\right]\ [\mathrm{J}]} = [\mathrm{m}]$$
$$\left[\frac{2\,\mathrm{e}^2\ (\mathrm{N_A})^2\ \rho_1^*(\ell)}{\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{R\,T}}\right]^{1/2} = \left[\frac{[1]\,[\mathrm{C}]^2\ \left[\mathrm{mol}^{-1}\right]^2\ \left[\mathrm{kgm}^{-3}\right]}{\left[\mathrm{Fm}^{-1}\right]\ [1]\ \left[\mathrm{Jmol}^{-1}\ \mathrm{K}^{-1}\right]\ [\mathrm{K}]}\right]^{1/2}$$
$$= \left[\frac{\left[\mathrm{A}^2\ \mathrm{s}^2\right]\ \left[\mathrm{mol}^{-1}\right]^2\ \left[\mathrm{kgm}^{-3}\right]}{\left[\mathrm{AsJAs}^{-1}\right]\ \left[\mathrm{Jmol}^{-1}\right]}\right]^{1/2} = \left[\left[\mathrm{mol}^{-1}\right]\ [\mathrm{kg}]\ \left[\mathrm{m}^{-2}\right]\right]^{1/2}$$
$$= \frac{\left[\mathrm{m}^{-1}\right]}{\left[\mathrm{molkg}^{-1}\right]^{1/2}}$$
$$\kappa\,\mathrm{a_j} = \left[\mathrm{m}^{-1}\right]\ [\mathrm{m}] = [1]$$
$$\frac{\mathrm{z_+\,z_-\,e^2}}{8\,\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{k\,T}}\left[\frac{2\,\mathrm{e}^2\ (\ \mathrm{N_A})^2\ \rho_1^*(\ell)}{\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{R\,T}}\right]^{1/2}\ \frac{(\mathrm{I})^{1/2}}{1+\kappa\,\mathrm{a_j}}$$
$$= [\mathrm{m}]\,\frac{\left[\mathrm{m}^{-1}\right]}{\left[\mathrm{molkg}^{-1}\right]^{1/2}}\,\frac{\left[\mathrm{molkg}^{-1}\right]^{1/2}}{[1]} = [1]$$

As required $\ln(\gamma_\pm) = [1]$

[20] J. S. Winn, Physical Chemistry, Harper Collins, New York, 1995,page 315.

[21] M. L. McGlashan, Chemical Thermodynamics, Academic Press, 1979, p 304.

[22] Using

a. $\rho_1^*(\mathrm{H_2O};\ell;2981.5\ \mathrm{K}) = 997.0474$; G.S.Kell, J. Chem. Eng.Data, 1975,20,97.
b. $\varepsilon_\mathrm{r}(\mathrm{H_2O};\ell;2981.5\ \mathrm{K}) = 78.36 \pm 0.05$ H. Kienitz and K. N. Marsh, Pure Appl. Chem.,1981,**53**,1874.
c. CODATA 1986 fundamental constants

[23] N. K. Adam, Physical Chemistry, Oxford, 1956, page 395.

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SECTION OVERVIEW

1.6: Composition

1.6.1: Composition- Mole Fraction- Molality- Concentration

1.6.2: Composition- Scale Conversions- Molality

1.6.3: Composition- Scale Conversion- Solvent Mixtures

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1.6.1: Composition- Mole Fraction- Molality- Concentration

A solution comprises at least two different chemical substances where at least one substance is in vast molar excess. The term 'solution' is used to describe both solids and liquids. Nevertheless the term 'solution' in the absence of the word 'solid' refers to a liquid. Chemists are particularly expert at identifying the number and chemical formulae of chemical substances present in a given closed system. Here we explore how the chemical composition of a given system is expressed. We consider a simple system prepared using water(ℓ) and urea(s) at ambient temperature and pressure. We designate water as chemical substance 1 and urea as chemical substance j, so that the closed system contains an aqueous solution. The amounts of the two substances are given by $\mathrm{n}_j\,(=\mathrm{w}_1/\mathrm{M}_1)$ and $\mathrm{n_j}\,(=\mathrm{w_j}/\mathrm{M_j})$ where w_1 and w_j are masses; M_1 and M_j are the molar masses of the two chemical substances. In these terms, n_1 and n_j are extensive variables.

$$\text{Mass of solution, } \mathrm{w} = \mathrm{n}_1\,\mathrm{M}_1 + \mathrm{n_j}\,\mathrm{M_j}$$

$$\text{Mass of solvent, } \mathrm{w}_1 = \mathrm{n}_1\,\mathrm{M}_1$$

For water, $\mathrm{M}_1 = 0.018\ \mathrm{kgmol}^{-1}$. However in reviewing the properties of solutions, chemists prefer intensive composition variables.

Mole Fraction

The mole fractions of the two substances x_1 and x_j are given by the following two equations:

$$\mathrm{x}_1 = \mathrm{n_l}/\left(\mathrm{n}_1 + \mathrm{n_j}\right) \quad \mathrm{x_j} = \mathrm{n_j}/\left(\mathrm{n}_1 + \mathrm{n_j}\right)$$

Here $x_1 + x_j = 1.0$. In general terms for a system comprising i-chemical substances, the mole fraction of substance k is given by equation (d).

$$\mathrm{x_k} = \mathrm{n_k}/\sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{n_j}$$

Hence $\sum_{j=1}^{j=i} x_j = 1.0$. The advantage of the dimensionless mole fraction scale is that in the absence of chemical reaction, the mole fraction $\mathrm{x_k}$ of chemical substance k is independent of both temperature and pressure.

Molality

For liquid systems, the chemical substance in vast excess is called the solvent whereas the other substances are called solutes. In the urea + water system, water is the solvent if $\mathrm{n}_1 >> \mathrm{n_j}$. We as observers of the properties of this system draw a distinction between the two substances, identifying urea as the **solute**. The molality of solute m_j is given by the amount of solute in $1\ \mathrm{kg}$ of solvent [1,2].

$$\mathrm{m_j} = \mathrm{n_j}/\mathrm{w}_1$$

Because the molality of solute j is defined in terms of masses of solute and solvent, m_j is independent of temperature and pressure. Hence for precise characterization of the properties of solutes the molality scale is preferred [2].

Concentration

The concentration of chemical substance j in a system volume V,

$$c_j = n_j/V$$

The latter statement is quite general. However chemists interested in the properties of solutions normally use the term 'concentration' with reference to the properties of a solute, substance j. Several problems are associated with equation (f). The major problem is that the volume of a solution depends on both temperature and pressure so both these intensive variables should be stated when c_j is quoted. A further problem emerges when there is a need to specify the precise composition of a given solution. Many chemists prepare a solution by dissolving a known mass of solute j in small volume of solvent. The volume of the solution is then 'made up to the mark' for a given volume (e.g. $250\ \mathrm{cm}^3$). But often chemists do not record precisely how much solvent is used. In these terms we see why the molality is often the preferred composition scale for solutions because the amounts of solvent and solute are precisely defined. However when thinking about the properties of solutions, chemists consider the distance between

solute molecules rather than their masses. An interesting calculation offers insight into the dependence of intermolecular separation for solutes as a function of solute concentration, $c_{j\_}$ [2-4]. As the concentration of the solute (e.g. urea) in an aqueous solution increases so the mean distance between the solute molecules decreases. In the event that the solute is a 1:1 salt (e.g. potassium bromide, KBr), the calculation takes account of the fact that each mole of salt produces, with complete dissociation two moles of solute ions [3,4]. We gain insight into the problem by considering a solution of $\mathrm{KBr(aq, 1\ moldm^{-3})}$. The calculated distance between ion centres is $0.94\ \mathrm{nm}$. The radii of these ions are approx. $0.15\ \mathrm{nm}$. The diameter of a water molecule is around $0.4\ \mathrm{nm}$. [5]. So there are relatively few water molecules between the ions at this concentration.

These calculations are important because they indicate how solute-solute distances change on increasing the concentration of solute. [6] Chemists often want to know how solute - solute molecular interactions affect the properties of solutions. [7-11] Certainly the distance between solute molecules is a key consideration in reviewing the properties of solutes in aqueous solutions. The task of understanding the properties of aqueous solutions is usually divided into two parts. For the first part we use the term hydration to describe solute - solvent interactions. We imagine a molecule of solute, chemical substance j, in an infinite expanse of solvent and direct attention to the organisation of solvent molecules surrounding each solute molecule, the cosphere. [7] The term hydration number often refers to the number of water molecules contiguous to each solute molecule but the term 'hydration shell' often extends to include solvent molecules outside the immediate sheath.

With increase in solute concentration the mean separation between solute molecules decreases. In responding to the task of understanding the properties of real solutions we define the properties of ideal solutions [10]. In the case of salt solutions, strong and long - range ion - ion interactions contribute to marked deviations from the properties of ideal solutions [11].

Footnotes

[1] $\mathrm{m_j = [molkg^{-1}]}$

[2] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd edn. revised, 1965, page 15.

[3] Consider a solution in which each solute molecule is placed at the centre of a cube, edge d metres. Then distance between solute molecules/$\mathrm{m} = \mathrm{d}$ Volume of one $textcube/\mathrm{m}^3 = \mathrm{d}^3$; Volume of n_j moles of cubes \(/\mathrm{m}^{3} = \mathrm{n}_{j} \,s \mathrm{N}_{\mathrm{A} \,s \mathrm{d}^{3}\) where \mathrm{N}_{\mathrm{A}}\) is the Avogadro constant. Thus $V(s\,\mathrm{ln}) = n_j\ N_A\ d^3$ or $d = (c_j\, N_A)^{-1/3}$ where c_j is expressed in $\mathrm{molm^{-3}}$. $\mathrm{d} = \left\{[\mathrm{molm^{-3}}]\ [\mathrm{mol^{-1}}]\right\}^{-1/3} = [\mathrm{m}]$ If c_j is expressed, as is conventional, in $\mathrm{moldm^{-3}}$, $\mathrm{d} = \left(10^3\, \mathrm{c_j\, N_A}\right)^{-1/3}$.

[4]

$\mathrm{c_j/moldm^{-3}}$	Single Solute d/nm	1 : 1 salt d/nm
10^{-4}	25.5	20.2
10^{-3}	11.8	9.4
10^{-2}	5.5	4.4
10^{-1}	2.6	2.0
1	1.2	0.94
5	0.69	0.55

[5] N. E. Dorsey, Properties of Ordinary Water Substance, Reinhold, New York, 1940. The estimate quoted in the main text is based on the estimates given in Table 15 of this fascinating monograph. The latter offers information concerning, for example, the load which ice will support. Apparently, ice having a thickness of 20 cm will support a battery of artillery with carriages and horses (see p. 458).

[6] Molalities are based on mass, and concentrations on distances.

[7] R. W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.

[8] H. L. Friedman and C. V. Krishnan,in Water - A Comprehensive Treatise, ed. F. Franks, Plenum Press, New York, 1973, Vol. 3, Chapter 1.

[9] J.-Y. Huot and C. Jolicoeur, in The Chemical Physics of Solvation, Part (a) Theory of Solvation,ed. J.Ulstrup, Elsevier, New York, 1985.

[10] One interesting feature is common throughout aqueous chemistry. If a given water molecule is strongly hydrogen bonded to four other water molecules, that water molecule exists in a local state which has low density (high volume). In other words, strong cohesion implies low density; a pattern contrary to that encountered in nearly all natural systems (and in human activities); A. Ben-Naim, Chem. Phys. Lett., 1972,**13**, 406. [Exceptions to this statement are found in the structures of high pressure ice polymorphs - but then there are always exceptions to general statements.]

[11] The seminal paper in this subject, aqueous chemistry, is probably that written by J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1933,1, 515. This paper is remarkable in that despite the subjects covered (i.e. ice, liquid water and aqueous solutions), the term 'hydrogen-bond' is not used. The authors refer to the tendency of water to group in 'tetrahedral coordination'.

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1.6.2: Composition- Scale Conversions- Molality

For a solution in a single solvent, chemical substance 1, containing solute j,

$$\text{Molaity, } \mathrm{m_j} = \mathrm{n_j}/\mathrm{w_1}$$

Here n_j is the amount of solute and w_1 is the mass of solvent [1]

Mole Faction and Molality

For the same system, the amount of solvent,

$$\mathrm{n_1} = \mathrm{n_j}/\mathrm{m_j}\,\mathrm{M_1}$$

But mole fraction, $\mathrm{x_j} = \mathrm{n_j}/\left(\mathrm{n_1} + \mathrm{n_j}\right)$

$$\text{Thus} \quad x_j = \frac{m_j\, n_1\, M_1}{n_1 + m_j\, n_1\, M_1} \quad \text{or} \quad x_j = \frac{m_j\, M_1}{1 + m_j\, M_1}$$

For dilute solutions, $1 >> m_j\, M_1$.

$$\text{Then } x_j = m_j\, M_1$$

For water(ℓ), $\mathrm{M_1} = 0.018 \text{ kg mol}^{-1}$. From equation (c) $x_j + x_j\, m_j\, M_1 = m_j\, M_1$

$$\text{Then} \quad x_j = m_j\, M_1\, (1 - x_j) \quad \text{or} \quad m_j = x_j/\left[M_1\, (1 - x_j)\right]$$

For dilute solutions $1 - x_j \approx 1.0$. and we recover equation (d). In short, equations (c) and (e) provide exact conversions between m_j and x_j whereas equation (d) is only valid for dilute solutions.

Concentration and Molality

We consider a solution having volume $\mathrm{V(sln)}$. Mass of solution $= \rho(s\,\mathrm{ln})\; V(s\,\mathrm{ln})$ where (at defined T and p), density $= \rho(\mathrm{sln})$. If amount of substance j in this solution is n_j mol then mass of solute $\mathrm{w_j} = \mathrm{n_j}\,\mathrm{M_j}$, where $\mathrm{M}_j =$ molar mass of solute.

Mass of solvent in system $= \rho(s\,\mathrm{ln})\, V(s\,\mathrm{ln}) - n_j\, M_j$

$$\text{Hence molality} \quad m_j = \frac{n_j}{\rho(s\,\mathrm{ln})\, V(s\,\mathrm{ln}) - n_j\, M_j}$$

$$\text{and concentration} \quad c_j = \frac{n_j}{V(s\,\mathrm{ln})}$$

From (f) and (g) $\mathrm{m_j} = \frac{\mathrm{n_j}}{\frac{\rho(s\,\mathrm{ln})\;\mathrm{n_j}}{\mathrm{c_j}} - \mathrm{n_j}\,\mathrm{M_j}} = \frac{1}{\frac{\rho(s\,\mathrm{ln})}{\mathrm{c_j}} - \mathrm{M_j}}$

$$\text{Or, } m_j = \frac{c_j}{\rho(s\,\mathrm{ln}) - M_j\, c_j}$$

$$\text{Or,} \quad c_j = \frac{m_j\, \rho(s\,\mathrm{ln})}{1 + m_j\, M_j}$$

For dilute solutions $\rho(\mathrm{s\,ln}) >> \mathrm{M_j\,c_j}$.

$$\text{Then[2] } c_j(s\,\mathrm{ln}) = m_j\, \rho(s\,\mathrm{ln})$$

Therefore the exact conversion is given by equations (h) and (i) which reduce to equation (j) for dilute solutions.

Molality and Concentration

An elegant conversion is possible between m_j and c_j scales. The volume of a simple solution is given by equation (k).

$$\mathrm{V(aq)} = \mathrm{n_1}\, \mathrm{V_1^*}(\ell) + \mathrm{n_j}\, \phi\, (\mathrm{V_j})$$

Here $\phi\,(\mathrm{V_j})$ is the apparent molar volume of solute j.

$$\text{Or,} \quad V(aq)/n_j = (n_1/n_j)\ [M_1/\rho_1^*(\ell)] + \phi\,(V_j)$$

$$\text{Or,} \quad 1/c_j = [1/m_j\ \rho_1^*(\ell)] + \phi\,(V_j)$$

$$\text{Then,}\ 1/m_j = [\rho_1^*(\ell)/c_j] - [\phi\,(V_j)\ \rho_1^*(\ell)]$$

Footnotes

[1] Amount of solvent, molar mass M_1, $n_1 = w_1/M_1$ Then, $m_j = n_j/n_1\,M_1$ Units $m_j = n_j/n_1\,M_1 = [\text{mol}]/[\text{mol}]\ \left[\text{kgmol}^{-1}\right] = \left[\text{molkg}^{-1}\right]$

[2] $c_j = [\text{molm}^{-3}] = \left[\text{molkg}^{-1}\right]\ [\text{kgm}^{-3}]$

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1.6.3: Composition- Scale Conversion- Solvent Mixtures

A given mixed solvent is prepared (at fixed T and p) by mixing $\mathrm{n}_1\,\mathrm{V}_1^*(\ell)\mathrm{m}^3$ of liquid 1 and $\mathrm{n}_2\,\mathrm{V}_2^*(\ell)\mathrm{m}^3$ of liquid 2. We will assume that the thermodynamic properties of the mixture are ideal.

$$\text{Then volume } \mathrm{V} = \mathrm{n}_1\,\mathrm{V}_1^*(\ell) + \mathrm{n}_2\,\mathrm{V}_2^*(\ell)$$

Then volume% of liquid 2 in the mixture is given by equation (b).

$$\mathrm{V}_2\% = \left[10^2\,\mathrm{n}_2\,\mathrm{V}_2^*(\ell)\right] / \left[\mathrm{n}_1\,\mathrm{V}_1^*(\ell) + \mathrm{n}_2\,\mathrm{V}_2^*(\ell)\right]$$

The mass of a given mixed solvent system equals $\mathrm{w_s}$. Further mass% of liquid 2 is w_2%.

$$\text{Thus } \mathrm{w}_2\% = \mathrm{w}_2\,10^2/\left(\mathrm{w}_1 + \mathrm{w}_2\right)$$

$$\text{Mole fraction } \mathrm{x}_2 = \left(\mathrm{w}_2\%/\mathrm{M}_2\right) / \left[\frac{\left(10^2 - \mathrm{w}_2\%\right)}{\mathrm{M}_1} + \frac{\mathrm{w}_2\%}{\mathrm{M}_2}\right]$$

$$\text{Also } \mathrm{V}_2\%(\text{mix; id }) = \left[10^2\,\mathrm{w}_2/\rho_2^*(\ell)\right] / \frac{\mathrm{w}_1}{\rho_1^*(\ell)} + \frac{\mathrm{w}_2}{\rho_2^*(\ell)}\Bigg]$$

If $\left(\mathrm{w}_1 + \mathrm{w}_2\right) = 100$ kg,

$$\mathrm{V}_2\%(\text{mix; id}) = \left[10^2\,\mathrm{w}_2\%/\rho_2^*(\ell)\right] / \left[\frac{\left(10^2 - \mathrm{w}_2\%\right)}{\rho_1^*(\ell)} + \frac{\mathrm{w}_2\%}{\rho_2^*(\ell)}\right]$$

Molality and Mole fraction

A given solvent mixture has mass 10^2 kg is prepared using w_2 kg $[= \mathrm{w}_2\%]$ of liquid 2; nj moles of solute are dissolved in this mixture.

$$\text{Molality } \mathrm{m_j/molkg^{-1}} = \mathrm{n_j}/10^2$$

$$\text{Mole fraction, } \mathrm{x_j} = \mathrm{n_j}/\left\{\left[\left(10^2 - \mathrm{w}_2\%\right)/\mathrm{M}_1\right] + \left[\mathrm{w}_2\%/\mathrm{M}_2\right] + \mathrm{n_j}\right\}$$

For dilute solutions, $\mathrm{n_j} << \left(\mathrm{n}_1 + \mathrm{n}_2\right)$

$$\text{Then, } \quad \mathrm{x_j} = \mathrm{n_j}/\left\{\left[\left(10^2 - \mathrm{w}_2\%\right)/\mathrm{M}_1\right] + \left[\mathrm{w}_2\%/\mathrm{M}_2\right]\right\}$$

$$\text{Or, } \quad \mathrm{x_j} = 10^2\,\mathrm{m_j}/\left\{\left[10^2 - \mathrm{w}_2\%\right]/\mathrm{M}_1\right] + \left[\mathrm{w}_2\%/\mathrm{M}_2\right]\}$$

Concentration and Molality

A given solution is prepared (at fixed T and p) using n_1 moles of liquid 1, n_2 moles of liquid 2 and n_j moles of a simple solute (e.g. urea) where $n_j << \left(n_1 + n_2\right)$.

$$\text{Mass of mixed solvent } \mathrm{w_s} = \mathrm{n}_1\,\mathrm{M}_1 + \mathrm{n}_2\,\mathrm{M}_2$$

$$\text{Mass of system, } w = n_j\,M_j + n_1\,M_1 + n_2\,M_2$$

$$\text{Molality of solute } \mathrm{m_j} = \mathrm{n_j}/\left[\mathrm{n}_1\,\mathrm{M}_1 + \mathrm{n}_2\,\mathrm{M}_2\right] = \mathrm{n_j}/\left[\mathrm{w}_1 + \mathrm{w}_2\right]$$

$$\text{Or, } \quad \mathrm{m_j} = \mathrm{n_j}/\mathrm{w_s}$$

Density of solution $= \rho$ Mass of solution $= \mathrm{w}$

$$\text{Volume of solution } \mathrm{V} = \left[\mathrm{n_j}\,\mathrm{M_j} + \mathrm{n}_1\,\mathrm{M}_1 + \mathrm{n}_2\,\mathrm{M}_2\right]/\rho$$

$$\text{Concentration of solute } j, \mathrm{c_j} = \mathrm{n_j}\,\rho/\left[\mathrm{n_j}\,\mathrm{M_j} + \mathrm{n}_1\,\mathrm{M}_1 + \mathrm{n}_2\,\mathrm{M}_2\right]$$

$$\text{For dilute solutions, } \mathrm{n_j}\,\mathrm{M_j} \ll \left[\mathrm{n}_1\,\mathrm{M}_1 + \mathrm{n}_2\,\mathrm{M}_2\right]$$

$$\text{Then, } \mathrm{c_j} \cong \mathrm{n_j}\,\rho/\left[\mathrm{n}_1\,\mathrm{M}_1 + \mathrm{n}_2\,\mathrm{M}_2\right]$$

If the solution is dilute, the density of the solution is approx. equal to density of the solvent ρ_s at the same T and p.

$$\text{Hence } \mathrm{c_j} \cong \mathrm{n_j}\,\rho_s / \left[\mathrm{n_1}\,\mathrm{M_1} + \mathrm{n_2}\,\mathrm{M_2}\right]$$

$$\text{Molality of solute } \mathrm{m_j} = \mathrm{n_j} / \left[\mathrm{n_1}\,\mathrm{M_1} + \mathrm{n_2}\,\mathrm{M_2}\right]$$

Then $c_j \cong m_j\, p_s$

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1.7.1: Compressions and Expansions- Liquids

The isothermal compressions of solutions and liquids have been extensively studied and the subject has a remarkable history. The term compression, symbol K describes the sensitivity of the volume of a system to an isothermal change in pressure, $(\partial V/\partial p)$. Reference is usually made to the voyage made by HMS Challenger and the report of experiments undertaken by Tait into the compression of water [1-3]. Kell summarises various equations which have been proposed describing the isothermal dependence of the molar volume of water on pressure [4]; see also references [5,6].

The dependence of the volume of water(ℓ) at low pressures and at a given temperature on pressure can be represented by equation (a) where A and B are constants.

$$[\mathrm{V}(\text{ ref }) - \mathrm{V}]/\mathrm{V}(\text{ ref })\,\mathrm{p} = \mathrm{A}/(\mathrm{B} + \mathrm{p})$$

Here $\mathrm{V}(\mathrm{ref})$ is the volume 'at zero pressure', usually ambient pressure (i.e. approx $105\ \mathrm{Nm}^{-2}$). This equation often called the Tait equation [4] has the form shown in equation (b).

$$-\left(1/\mathrm{V}^{0}\right)\ (\partial \mathrm{V}/\partial \mathrm{p}) = \mathrm{A}/(\mathrm{B} + \mathrm{p})$$

$$\text{Alternatively [4] } \mathrm{V} = \mathrm{V}^{0}\{1 - \mathrm{A}\ \ln[(\mathrm{B} + \mathrm{p})/\mathrm{B}]\}$$

The challenge of measuring the isothermal compression of liquids has been taken up by many investigators; e.g. references [7-12]. The isothermal compressions of a liquid K_{T} is defined by equation (d) [13].

$$\mathrm{K}_{\mathrm{T}} = -(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T}}$$

The isothermal compressibility is given by equation (e) [14].

$$\kappa_{\mathrm{T}} = -\mathrm{V}^{-1}\,(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T}}$$

For all thermodynamic equilibrium states, both K_{T} and κ_{T} are positive variables. A related variable is the isochoric thermal pressure coefficient, $(\partial p/\partial T)_{v}$.[15]

We develop the story in the context of systems containing two liquid components. For a closed system containing n_1 and n_2 moles of chemical substances 1 and 2, the Gibbs energy is a dependent variable and the variables $[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2]$ are the independent variables. Temperature T is the thermal potential; pressure p is the mechanical variable. The number of thermodynamic variables necessary to define the system is established using the Gibbs Phase Rule [16]. For a closed system (at defined T and p) at thermodynamic equilibrium the composition/organisation is represented by ξ^{eq}. The affinity for spontaneous change is zero consistent with the Gibbs energy being a minimum; equation (f).

$$\mathrm{A} = -(\partial \mathrm{G}/\partial \xi)^{\mathrm{eq}}_{\mathrm{T,p}} = 0$$

The Gibbs energy, volume and entropy of a solution at equilibrium are state variables. We contrast these properties with those properties which are associated with a process (pathway). Thus we contrast the state variable V with an unspecified compression of a solution. We need to define the path followed by the system when the pressure is changed. The Gibbs energy of a closed system at thermodynamic equilibrium (where the affinity for spontaneous change is zero and where the molecular composition/organisation is characterised by ξ^{eq}) is described by equation (g).

$$\mathrm{G} = \mathrm{G}\,[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2,\ \mathrm{A} = 0]$$

The same state is characterised by the equilibrium volume and equilibrium entropy by equations (h) and (i) respectively.

$$\mathrm{V} = \mathrm{V}\,[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2,\ \mathrm{A} = 0]$$

$$\mathrm{S} = \mathrm{S}\,[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2,\ \mathrm{A} = 0]$$

We use two intensive variables, T and p, in the definition of extensive variables G, V and S. When the pressure is increased by finite increments from p to $(\mathrm{p} + \Delta \mathrm{p})$, the volume changes in finite increments from V to $(\mathrm{V} + \Delta \mathrm{V})$. For an important pathway, the temperature is constant. However to satisfy the condition that the affinity for spontaneous change A is zero, the molecular organisation/composition ξ changes. The volume at pressure $(\mathrm{p} + \Delta \mathrm{p})$ is defined using equation (j).

$$V = V\,[T, (p + \Delta p), n_1, n_2,\ A = 0]$$

In principle we plot the volume as a function of pressure at constant temperature, n_1, n_2, and at '$A = 0$'. The gradient of the plot defined by equation (h) yields the equilibrium isothermal compression, $K_T(A = 0)$; equation (k)

$$K_T(A = 0) = -(\partial V/\partial p)_{T,A=0}$$

$K_T(A = 0)$ characterises the state defined by the set of variables, $[T, p, n_1, n_2,\ A = 0]$.

We turn our attention to another property starting with a system having a volume defined by equation (h). The system is perturbed by a change in pressure from p to $(p + \Delta p)$ in an equilibrium displacement. However on this occasion we require that the entropy of the system remains constant at a value defined by equation (i). In principle we plot the volume V as a function of pressure at constant n_1, n_2, at '$A = 0$' and at a constant entropy defined by equation (i). The gradient of the plot at the point where the volume is defined by equation (g) yields the equilibrium isentropic compression $K_S(A = 0)$; equation (l) where isentropic = adiabatic and 'at equilibrium'.

$$K_S(A = 0) = -(\partial V/\partial p)_{S,A=0}$$

The equilibrium state characterised by $K_S(A = 0)$ is defined by the variables $[T, p, n_1, n_2,\ A = 0]$. In other words an isentropic volumetric property describes a solution defined in part by the intensive variables T and p. Significantly the condition on the partial derivative in equation (l) is an extensive variable, entropy. For a stable phase K_S is positive.

The arguments outlined above are repeated with respect to both isobaric equilibrium expansions $E_p(A = 0)$ and isentropic equilibrium expansions, $E_S(A = 0)$; equations (m) and (n).

$$E_p(A = 0) = -(\partial V/\partial T)_{p,A=0}$$

$$E_S(A = 0) = -(\partial V/\partial T)_{S,A=0}$$

The (equilibrium) volume intensive isothermal κ_T and isentropic κ_S compressibilities are defined by equations (o) and (p) .

$$\kappa_T = -(1/V)\,(\partial V/\partial p)_T = K_T\,V^{-1}$$

$$\kappa_s = -(1/V)\,(\partial V/\partial p)_s = K_s\,V^{-1}$$

In 1914 Tyrer reported isentropic and isothermal compressibilities for many liquids [9]. Equations (q) and (r) define two (equilibrium) expansibilities, isentropic and isobaric, volume intensive properties.

$$\alpha_s = (1/V)\,(\partial V/\partial T)_s = E_S\,V^{-1}$$

$$\alpha_p = (1/V)\,(\partial V/\partial T)_p = E_p\,V^{-1}$$

Rowlinson and Swinton state that the property α_S is 'of little importance' [17]. The isobaric heat capacity per unit volume σ is the ratio $[C_p/V]$. A property of some importance is the difference between compressibilities, δ; equation (s).

$$\delta = \kappa_T - \kappa_S = T\,[\alpha_p]^2\,V/C_p = T\,[\alpha_p]^2/\sigma$$

The property σ is given different symbols and names; e.g. volumetric specific heat. Here we identify σ as the thermal (or, heat) capacitance. The property ε is the difference between isobaric and isentropic expansibilities; equation (t).

$$\varepsilon = \alpha_p - \alpha_s = \kappa_T\,\sigma/T\,\alpha_p$$

The Newton–Laplace equation is the starting point for the determination of isentropic compressibilities of liquids using sound speeds and densities; equation (u).

$$u^2 = (\kappa_s\,\rho)^{-1}$$

The isentropic condition on κ_S means that as a sound wave passes through a liquid the pressure and temperature fluctuate within each microscopic volume but the entropy remains constant.

Footnotes

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[12] D. N. Newitt and K.Weale, J.Chem. Soc.,1951,3092.

[13] $\mathrm{K_T} = [\mathrm{m^3}] \,/\, [\mathrm{Nm^{-2}}] = [\mathrm{m^3\ Pa^{-1}}]$

[14] $\mathrm{K_T} = \frac{1}{[\mathrm{\ m^3}]} \frac{[\mathrm{m^3}]}{[\mathrm{Pa}]} = [\mathrm{Pa^{-1}}]$

[15] $(\partial \mathrm{p}/\partial \mathrm{T})_\mathrm{V} = [\mathrm{PaK^{-1}}]$

[16] Phase Rule; $\mathrm{P} = 1$; $\mathrm{C} = 2$. Hence $\mathrm{F} = 3$. Then we define T, p and mole fraction composition.

[17] J. S. Rowlinson and F. L. Swinton, Liquids and Liquid Mixtures, Butterworths, London, 3rd edn., 1982, pp 16-17.

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1.7.2: Compressibilities (Isothermal) and Chemical Potentials- Liquids

The (equilibrium) isothermal compressibility of a closed system containing a condensed phase is given by equation (a).

$$\kappa_{\mathrm{T}} = -\frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

$$\text{Or,} \quad \kappa_{\mathrm{T}} = -\left(\frac{\partial \ln(\mathrm{V})}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

Here we assume that over a range of pressures of interest here , κ_{T} is independent of pressure.

$$\text{Hence at fixed temperature,} \int_{p=0}^{p} d\ln(V) = -K_T \int_{p=0}^{p} dp$$

We define a property $V(p=0)$, the volume of the system under consideration extrapolated to zero pressure at fixed temperature.

$$\text{Therefore } \ln[\mathrm{V(p)/V(p=0)}] = -\kappa_{\mathrm{T}}\,\mathrm{p}$$

$$\text{Or, } \mathrm{V(T,p)} = \mathrm{V(T,p=0)}\,\exp\left(-\mathrm{K_T\,p}\right)$$

For systems at ordinary pressures, $\kappa_{\mathrm{T}}\,\mathrm{P} << 1$.

$$\text{Hence [1] } \mathrm{V(T,p)} = \mathrm{V(T,p=0)}\,[1-\kappa_{\mathrm{T}}\,\mathrm{p}]$$

For example, in the case of a pure liquid , chemical substance 1 [e.g. water]

$$\mathrm{V_1^*(\ell;T;p)} = \mathrm{V_1^*(\ell;T,p=0)}\,[1-\kappa_{\mathrm{T1}}^*(\ell)\,\mathrm{p}]$$

$$\text{But for water } (\ell), \lfloor \partial\mu_1^*(\ell)/\partial \mathrm{p} \rfloor = \mathrm{V_1^*(\ell;T;p)}$$

$$\text{Hence} \quad \left[\frac{\partial \mu_1^*(\ell)}{\partial \mathrm{p}}\right] = \mathrm{V_1^*(\ell;T;p=0)}\,[1-\kappa_{\mathrm{T1}}^*(\ell)\,\mathrm{p}]$$

Or, following integration between limits '$\mathrm{p}=0$' and p,

$$\mu_1^*(\ell;\mathrm{T;p}) = \mu_1^*(\ell;\mathrm{T;p=0}) + \mathrm{p\,V_1^*(\ell;T;p=0)}\,[1-(1/2)\,\kappa_{\mathrm{T1}}^*(\ell)\,\mathrm{p}]$$

The latter equation relates the chemical potential of a liquid at pressure p to the isothermal compressibility of the liquid [2].

Footnote

[1] With $\exp(x) = 1 + x + (x^2/2!) + (x^3/3!) + \ldots\ldots$ At small x, $\exp(x) \approx 1 + x$

[2] I. Prigogine and R. Defay, Chemical Thermodynamics, transl D. H. Everett, Longmans Green, London, 1953.

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1.7.3: Compressions- Isentropic- Solutions- General Comments

At fixed T and p, the equilibrium state for an aqueous solution is a minimum in Gibbs energy, G^{eq}. The first derivative of G^{eq} with respect to temperature at constant pressure yields the equilibrium enthalpy H^{eq}. The first derivative of H^{eq} with respect to temperature also at constant pressure yields the equilibrium isobaric heat capacity ${\mathrm{C_p}}^{\mathrm{eq}}$. Alternatively we can track the pressure derivatives of G^{eq}. The first derivative of G^{eq} with respect to pressure at fixed temperature is the equilibrium volume V^{eq}. The first derivative of V^{eq} with respect to pressure at fixed temperature yields the equilibrium isothermal compression $\mathrm{K}_{\mathrm{T}}^{\mathrm{eq}}$, the ratio $\mathrm{K}_{\mathrm{T}}^{\mathrm{eq}}/\mathrm{V}^{\mathrm{eq}}$ yielding the equilibrium isothermal compressibility $\kappa_{\mathrm{T}}^{\mathrm{eq}}$. Concentrating attention on equilibrium properties of aqueous solutions, an extensive literature concerns $\mathrm{V(aq)}$ in terms of the corresponding densities, $\rho(\mathrm{aq})$. An extensive literature describes isobaric heat capacities $\mathrm{C_p(aq}$, effectively the second derivative of $\mathrm{G(aq}$. Rather less literature describes $\kappa_{\mathrm{T}}(\mathrm{aq}$, a second derivative of $\mathrm{G(aq)}$ with respect to pressure. However an extensive literature reports isentropic compressibilities, \(\kappa_{\mathrm{S}(\mathrm{aq})\); equation (a).

$$\kappa_{\mathrm{S}} = -(1/\mathrm{V})\,(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{S}} = \mathrm{K_S}\,\mathrm{V}^{-1}$$

This perhaps surprising observation is accounted for by the fact that speeds of sound (at low frequency, e.g. $1\ \mathrm{MHz}$) in aqueous solutions are conveniently and precisely measured using either the 'sing-around; [1] or 'pulse-echo-overlap' [2] methods {for a summary of the 'History of Sound' see reference 3.) Then using the Newton-LaPlace equation $\kappa_{\mathrm{S}}(\mathrm{aq})$ is obtained [5]; equation (b).

$$\mathrm{u}^2 = (\kappa_{\mathrm{s}}\,\rho)^{-1}$$

The speed of sound at zero frequency is a thermodynamically defined property [5,6]. The isentropic compressibility of water(ℓ) at ambient T and p can be calculated using either the speed of sound $\kappa_{\mathrm{s}}^{*}(\ell;\ \mathrm{acoustic}\ )$ or using $\kappa_{\mathrm{T}}^{*}(\ell)$, $\alpha_{\mathrm{P}}^{*}(\ell)$ and $\sigma^{*}(\ell)$ to yield $\kappa_{\mathrm{s}}^{*}(\ell;\ \mathrm{thermodynamic}\ )$. The two estimates agree lending support to the practice of calculating isentropic compressibilities of solutions using the Newton-Laplace equation. We equate the isentropic condition with adiabatic, provided that the compression is reversible.

An important quantity is the difference δ between compressibilities; equation (c).

$$\delta = \kappa_{\mathrm{T}} - \kappa_{\mathrm{S}} = \mathrm{T}\ (\alpha_{\mathrm{p}})^2\,/\sigma$$

The property σ is given a number of different names but here we use the term, heat (or, thermal) capacitance. The ratio of isothermal to isentropic compressions equals the ratio of isobaric to isochoric heat capacities [8].

$$\mathrm{K_T}/\mathrm{K_S} = \mathrm{C_p}/\mathrm{C_V}$$

Interest in the isentropic compressibilities of solutions was stimulated by Gucker and co-workers [9,10] and, in particular, by Harned and Owen [11]. The latter authors **defined** a property of the solute, here called $\phi\,(\mathrm{K_{Sj}};\ \mathrm{def}\ )$ using equation (e) where the composition of a given aqueous solution is expressed using concentration c_j.

$$\phi\,(\mathrm{K_{Sj}};\mathrm{def}) \equiv [\kappa_{\mathrm{S}}(\mathrm{aq}) - \kappa_{\mathrm{Sl}}^{*}(\ell)]\ [\mathrm{c_j}]^{-1} + \kappa_{\mathrm{S1}}^{*}(\ell)\,\phi\,(\mathrm{V_j})$$

Also

$$\phi\,(\mathrm{K_{Sj}};\mathrm{def}) \equiv \\ [\kappa_{\mathrm{S}}(\mathrm{aq})\,\rho_1^{*}(\ell) - \kappa_{\mathrm{Sl}}^{*}(\ell)\,\rho(\mathrm{aq})]\ [\mathrm{c_j}\,\rho_1^{*}(\ell)]^{-1} + \kappa_{\mathrm{S1}}^{*}(\ell)\,\mathrm{M_j}\ [\rho_1^{*}(\ell)]^{-1}$$

Similar equations relate $\phi\,(K_{\mathrm{Sj}};\ \mathrm{def}\ )$ to the molality of the solute, m_j.

$$\phi\,(\mathrm{K_{sj}};\mathrm{def}) \equiv [\kappa_{\mathrm{s}}(\mathrm{aq}) - \kappa_{\mathrm{s1}}^{*}(\ell)]\ [\mathrm{m_j}\,\rho_1^{*}(\ell)]^{-1} + \kappa_{\mathrm{s}}(\mathrm{aq})\,\phi\,(\mathrm{V_j})$$

$$\phi\,(\mathrm{K_{Sj}};\mathrm{def}) \equiv \\ [\kappa_{\mathrm{S}}(\mathrm{aq})\,\rho_1^{*}(\ell) - \kappa_{\mathrm{Sl}}^{*}(\ell)\,\rho(\mathrm{aq})]\ [\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_1^{*}(\ell)]^{-1} \\ + \kappa_{\mathrm{S}}(\mathrm{aq})\,\mathrm{M_j}\,[\rho(\mathrm{aq})]^{-1}$$

The latter four equations are stated by analogy with those relating $\phi\,(\mathrm{K_{Tj}})$ to the composition of a solution. In these terms equations (e) to (h) are said to describe the same property of a given solute. A crucial feature of equations (e) - (h) is the equivalence symbol (i.e.. $\equiv$). In this sense Harned and Owen [11] defined an apparent isentropic compression of solute-j in terms of the quantities on

the r.h.s. of equation (a). They recognised that $\phi\,(\mathrm{K_{Sj};\ def}\,)$ does not have thermodynamic basis. The target quantity is the apparent molar isentropic compression defined by equation (i) which, however, is not a description of an isentropic process as its name might suggest.

$$\phi\,(\mathrm{K_{sj};def}) = (1/\mathrm{n_j})\ \mathrm{K_s(aq;T;p)} - (\mathrm{n_1/n_j})\ \mathrm{K^*_{S1}}(\ell;\mathrm{T;p})$$

In fact $\phi\,(\mathrm{K_{Sj};def})$ is a measure of the change in the isentropic compression of a solvent when solute j is added under isothermal-isobaric conditions. The equivalence symbol in equations (e) - (h) is important [12,13]. In fact reservations are often expressed especially when estimates of $\phi\,(\mathrm{K_{Sj};\ def}\,)$ are discussed, particularly the dependence of $\phi\,(\mathrm{K_{Sj};\ def}\,)$ on solution composition. Franks and co-workers [14] recognised that the lack of isobaric heat capacity data forces the adoption of an approach in which $\phi\,(\mathrm{K_{Sj};\ def}\,)$ is often effectively assumed equal to $\phi\,(\mathrm{K_{Tj^i}})$. Owen and Simons [15] comment that overlooking the difference between $\kappa_\mathrm{S}(\mathrm{aq})$ and $\kappa_\mathrm{T}(\mathrm{aq})$ causes errors of approximately 7.5% in estimates of $\phi\,(\mathrm{K_{Tj}})^\infty$ for $\mathrm{NaCl(aq)}$ and $\mathrm{KCl(aq)}$ at $298\ \mathrm{K}$.

In terms of the development of the theory, a problem is encountered with the differential dependence of the molar volume of the solvent on pressure at constant entropy of the solution. The task is to describe how the molar volume of the solvent would depend on pressure if it were held at the same entropy of the solution.

Footnotes

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1.7.4: Compressibilities- Isentropic- Related Properties

A given closed system at temperature T and pressure p contains chemical substances 1 and j. The system at specified T and p is at equilibrium where the affinity for spontaneous change is zero. We describe the volume and the entropy of the system using the following two equations.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \mathrm{A} = 0\right]$$

$$\mathrm{S} = \mathrm{S}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \mathrm{A} = 0\right]$$

The system is perturbed by a change in pressure. We envisage two possible paths tracked by the system accompanying a change in volume. In the first case the temperature is constant along the path for which '$\mathrm{A} = 0$'. The isothermal equilibrium dependence of volume on pressure, namely the equilibrium isothermal compression $\mathrm{K_T}(\mathrm{A} = 0)$, is defined by equation (c).

$$K_T(A = 0) = -\left(\frac{\partial V}{\partial p}\right)_{T,A=0}$$

In the second case the entropy remains constant along the path travelled by the system where '$\mathrm{A} = 0$'. The differential equilibrium isentropic compression is given by equation (d); isentropic = adiabatic + equilibrium

$$\mathrm{K_s}(\mathrm{A} = 0) = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{S,A}=0}$$

For all stable phases the volume of a given system decreases with increase in pressure at fixed temperature. The minus signs in equations (c) and (d) mean that compressions are positive variables. Neither $\mathrm{K_T}(\mathrm{A} = 0)$ or $\mathrm{K_S}(\mathrm{A} = 0)$ are strong functions of state because both variables describe pathways between states. The partial differentials in equations (c) and (d) differ in an important respect. The isothermal condition refers to an intensive variable whereas the isentropic condition refers to an extensive variable. The two properties $\mathrm{K_T}(\mathrm{A} = 0)$ and $\mathrm{K_S}(\mathrm{A} = 0)$ are related using a calculus operation.

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{S,A}=0} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} - \left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} \left(\frac{\partial \mathrm{T}}{\partial \mathrm{S}}\right)_{\mathrm{p,A}=0} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P,A}=0}$$

Hence, [1]

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{S,A}=0} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} + \left[\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p,A}=0}\right]^2 \frac{\mathrm{T}}{\mathrm{C_p}(\mathrm{A} = 0)}$$

But the (equilibrium) isobaric expansibility,

$$\alpha_p(A = 0) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,A=0}$$

$$\text{Then } \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{S,A}=0} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} + \left[\alpha_\mathrm{p}(\mathrm{A} = 0)\right]^2 \frac{\mathrm{V}^2\,\mathrm{T}}{\mathrm{C_p}(\mathrm{A} = 0)}$$

By definition, the equilibrium isobaric heat capacity per unit volume [2] {also called heat capacitance [3]},

$$\sigma(A = 0) = C_p(A = 0)/V$$

In terms of compressions,

$$\mathrm{K_S}(\mathrm{A} = 0) = \mathrm{K_T}(\mathrm{A} = 0) - \left[\alpha_\mathrm{p}(\mathrm{A} = 0)\right]^2 \frac{\mathrm{V\,T}}{\sigma(\mathrm{A} = 0)}$$

Three terms in equation (j), $\mathrm{K_S}(\mathrm{A} = 0)$, $\mathrm{K_T}(\mathrm{A} = 0)$ and V, are volume extensive variables. However it is convenient to rewrite these equations using volume intensive variables. Two equations define the isentropic equilibrium compressibility $\kappa_\mathrm{S}(\mathrm{A} = 0)$ and isothermal equilibrium compressibility $\kappa_\mathrm{T}(\mathrm{A} = 0)$ of a given system.

$$\kappa_\mathrm{T}(\mathrm{A} = 0) = -\frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} = \frac{\mathrm{K_T}(\mathrm{A} = 0)}{\mathrm{V}}$$

$$\kappa_S(A=0) = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{s,A=0} = \frac{K_S(A=0)}{V}$$

$$\text{Therefore } \kappa_S(A=0) = \kappa_T(A=0) - [\alpha_p(A=0)]^2 \frac{T}{\sigma(A=0)}$$

$$\text{By definition, } \delta = \kappa_T - \kappa_S$$

$$\text{Then } \delta(A=0) = [\alpha_p(A=0)]^2 \frac{T}{\sigma(A=0)}$$

Footnotes

[1] From a Maxwell relationship for the condition at '$A = 0$'; i.e. at equilibrium, $\partial^2 G/\partial T\, \partial p = \partial^2 G/\partial p\, \partial T$. Then, $E_p = (\partial V/\partial T)_p = -(\partial S/\partial p)_T$ From the Gibbs - Helmholtz equation, we combine the equations, $H = G + T\, S$ and $S = -(\partial G/\partial T)_p$. Hence, $H = G - T\,(\partial G/\partial T)_p$ Then, $(\partial H/\partial T)_p = C_p = -T\,(\partial^2 G/\partial T^2)_p = T\,(\partial S/\partial T)_p$

[2] $\kappa_S(A=0) = [Pa]^{-1} \quad \kappa_T(A=0) = [Pa]^{-1}$

$[\alpha_p(\ A=0)]^2 \frac{T}{\sigma(A=0)} = \left[K^{-1}\right]^2 [K]\ \left[JK^{-1}\ m^{-3}\right]^{-1} = \left[Nm^{-2}\right]^{-1} = Pa^{-1}$

$\sigma(A=0) = C_p(A=0)/V = \left[JK^{-1}\right]\ [m]^{-3}$

[3] M. J. Blandamer, M. I. Davis, G. Douheret and J. C. R. Reis, Chem. Soc Rev., 2001, **30**,8.

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1.7.5: Compressions- Isentropic- Solutions- Partial and Apparent Molar

Isentropic properties of aqueous solutions are defined in a manner analogous to that used to define isothermal compressions and isothermal compressibilities. The assertion is made that a system (e.g. an aqueous solution) can be perturbed along a pathway where the affinity for spontaneous change is zero by a small change in pressure $\delta \mathrm{p}$, to a neighbouring state having the same entropy. The (equilibrium) isentropic compression is defined by equation (a).

$$\mathrm{K_S(aq)} = -[\partial \mathrm{V(aq)}/\partial \mathrm{p}]_{\mathrm{S(aq)},A=0}$$

The constraint on this partial differential refers to 'at constant $\mathrm{S(aq)}$'. The definition of $\mathrm{K_S(aq)}$ uses non-Gibbsian independent variables. In other words, isentropic parameters do not arise naturally from the formalism which expresses the Gibbs energy in terms of independent variables in the case of, for example, a simple solution, $[\mathrm{T}, \mathrm{p}, \mathrm{n_l}, \mathrm{n_j}]$ [1]. The isothermal compression of a solution $\mathrm{K_T(aq)}$ and partial molar isothermal compressions of both solvent $\mathrm{K_{T1}(aq)}$ and solute $\mathrm{K_{T}}_j\mathrm{(aq)}$ are defined using Gibbsian independent variables. Unfortunately the corresponding equations cannot be simply carried over to the isentropic property $\mathrm{K_S(aq)}$. The volume of a solution is expressed in terms of the amounts of solvent $\mathrm{n_1}$ and solute n_j.

$$\mathrm{V(aq)} = \mathrm{n_1\, V_1(aq)} + \mathrm{n_j\, V_j(aq)}$$

The latter equation is differentiated with respect to pressure at constant entropy of the solution $\mathrm{S(aq)}$. The latter condition includes the condition that the system remains at equilibrium where the affinity for spontaneous change is zero. We emphasize a point. The entropy which remains constant is that of the solution.

$$\mathrm{K_s(aq)} = -\mathrm{n_1}\ [\partial \mathrm{V_1(aq)}/\partial \mathrm{p}]_{\mathrm{S(aq);A=0}} - \mathrm{n_j}\ [\partial \mathrm{V_j(aq)}/\partial \mathrm{p}]_{\mathrm{S(aq);A=0}}$$

$\mathrm{K_S(aq)}$ is an extensive property of the aqueous solution. $\mathrm{K_S(aq)}$ may also be re-expressed using Euler's theorem as a function of the composition of the solution.

$$\mathrm{K_s(aq)} = \mathrm{n_1}\ [\partial \mathrm{K_s(aq)}/\partial \mathrm{n_1}]_{\mathrm{T,p,n(j)}} + \mathrm{n_j}\ [\partial \mathrm{K_s(aq)}/\partial \mathrm{n_j}]_{\mathrm{T,p,n(l)}}$$

Because $\mathrm{K_S(aq)}$ is defined using non-Gibbsian independent variables, two important inequalities follow.

$$-[\partial \mathrm{V_1(aq)}/\partial \mathrm{p}]_{\mathrm{S(aq)}} \neq [\partial \mathrm{K_s(aq)}/\partial \mathrm{n_1}]_{\mathrm{T,p,n(j)}}$$

$$-[\partial \mathrm{V_j(aq)}/\partial \mathrm{p}]_{\mathrm{S(aq)}} \neq [\partial \mathrm{K_S(aq)}/\partial \mathrm{n_j}]_{\mathrm{T,p,n(1)}}$$

$[\partial \mathrm{K_s(aq)}/\partial \mathrm{n_1}]_{\mathrm{T,p,n(j)}}$ and $[\partial \mathrm{K_S(aq)}/\partial \mathrm{n_j}]_{\mathrm{T,p,n(1)}}$ are respectively the partial molar properties of the solvent and solute. Because partial molar properties should describe the effects of a change in composition on the properties of a solution, we write equation (d) for an aqueous solution in the following form.

$$\mathrm{K_S(aq)} = \mathrm{n_1\, K_{S1}(aq;\ def\ )} + \mathrm{n_j\, K_{Sj}(aq;\ def\ )}$$

$$\text{Hence,} \quad \mathrm{K_{sj}(aq;\ def\ )} \neq -[\partial \mathrm{V_j(aq)}/\partial \mathrm{p}]_{\mathrm{S(aq)}}$$

In view of the latter inequality $\mathrm{K_{Sj}(aq;def)}$ is a non-Lewisian partial molar property [2]. We could define a molar isentropic compression of solute j as (minus) the isentropic differential dependence of partial molar volume on pressure. This alternative definition is consistent with equation (g) expressing a summation rule analogous to that used for partial molar properties. However some other thermodynamic relationships involving partial molar properties would not be valid in this case. Therefore, $-[\partial V_j(aq)/\partial p]_{S(aq)}$ is a semi-partial molar property. A similar problem is encountered in defining an apparent molar compression for solute j, $\phi\left(\mathrm{K_{S_j}}\right)$ in a solution where the solute has apparent molar volume $\phi\left(\mathrm{V_j}\right)$; cf. equation (h) [3,4]. We might assert that $\phi\left(\mathrm{K_{S_j}}\right)$ is related to the isentropic differential dependence of $\phi\left(\mathrm{V_j}\right)$ on pressure, $-\left[\phi\left(\mathrm{V_j}\right)/\mathrm{p}\right]_{\mathrm{S(aq)}}$. Alternatively, using as a guide the apparent molar properties $\phi\left(\mathrm{E_{pj}}\right)$ and $\phi\left(\mathrm{K_{T}}^{\mathrm{j}}\right)$, we could define $\phi\left(\mathrm{K_{Sj};def}\right)$ using equation (i).

$$\mathrm{K_S(aq)} = \mathrm{n_1\, K^*_{S1}(l)} + \mathrm{n_j}\, \phi\left(\mathrm{K_{Sj};\ def\ }\right)$$

$\mathrm{K_{Sj}(aq;def)}$ as given by equation (d) and $\phi\left(K_{Sj};\ \mathrm{def}\ \right)$ are linked; equation (j).

$$\mathrm{K_{Sj}(aq;def)} = \phi\left(\mathrm{K_{Sj};def}\right) + \mathrm{n_j}\ [\partial \phi\left(\mathrm{K_{Sj};\ def\ }\right)/\partial \mathrm{n_j}]_{\mathrm{T,p,n(l)}}$$

Equation (j) is of the general form encountered for other apparent and partial molar properties. This form is also valid in the case of partial and apparent molar isobaric expansions, isothermal compressions and isobaric heat capacities. On the other hand, the semi-partial molar isentropic compression defined by $-\left[\partial \mathrm{V_j(aq)}/\partial \mathrm{p}\right]_{\mathrm{s(aq)}}$ and the semi-apparent molar isentropic compression defined by $-\left[\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{p}\right]_{\mathrm{S(aq)}}$ are related. The isentropic pressure dependence of $\mathrm{V_j(aq)}$ is given by equation (k).

$$-\left[\partial \mathrm{V_j(aq)}/\partial \mathrm{p}\right]_{\mathrm{S(aq)}} = \\ -\left[\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{p}\right]_{\mathrm{S(aq)}} - \mathrm{n_j}\left\{\partial\left[\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{n_j}\right]_{\mathrm{T,p,n(l)}}/\partial \mathrm{p}\right\}_{\mathrm{s(aq)}}$$

However,

$$\left\{\partial\left[\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{n_j}\right]_{\mathrm{T,p,n(1)}}/\partial \mathrm{p}\right\}_{\mathrm{S(aq)}} \neq \left\{\partial\left[\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{p}\right]_{\mathrm{S(aq)}}/\partial \mathrm{n_j}\right\}_{\mathrm{T,p,n(1)}}$$

Hence, the analogue of equation (j) does not hold for these 'semi' properties. The inequalities (e) and (f) highlight the essence of non-Lewisian properties. Their origin is a combination of properties defined in terms of Gibbsian and non-Gibbsian independent variables as in equations (e) and (f). This combination is also the reason for the inequality (l). We stress that the isentropic condition in equations (e) and (f) refers to the entropy $\mathrm{S(aq)}$ of the solution defined as is the volume $\mathrm{V(aq)}$ by the Gibbsian independent variables $[\mathrm{T, p, n_1, n_j}]$. But this is not the entropy $\mathrm{S_1^*(\ell)}$ of the pure solvent having volume $\mathrm{V_1^*(\ell)}$. $\mathrm{S(aq)}$ at fixed composition is not simply related to $\mathrm{S_1^*(\ell)}$ as, for example, linear functions of temperature and pressure.

The isentropic condition is involved in the definitions of isentropic compression, $\mathrm{K_{S1}^*(\ell)}$ and isentropic compressibility $\kappa_{\mathrm{S1}}^*(\ell)$ of the solvent.

$$\mathrm{K_{S1}^*(\ell)} = -\left[\partial \mathrm{V_1^*(\ell)}/\partial \mathrm{p}\right] \text{ at constant } \mathrm{S_1^*(\ell)}$$

$$\kappa_{\mathrm{Sl}}^*(\ell) = \mathrm{K_{Sl}^*(\ell)}/\mathrm{V_1^*(\ell)} \\ = -\left[\partial \mathrm{V_1^*(\ell)}/\partial \mathrm{p}\right]/\mathrm{V_1^*(\ell)} \text{ at constant } \mathrm{S_1^*(\ell)}$$

The different isentropic conditions in equation (a) and in equations (m) and (n) signal a complexity in the isentropic differentiation of equation (o) with respect to pressure [5,6].

$$\mathrm{V\left(aq; w_1 = 1\ kg\right)} = \mathrm{M_1^{-1}\, V_1^*(\ell)} + \mathrm{m_j}\, \phi\left(\mathrm{V_j}\right)$$

Footnotes

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1.7.6: Compressions- Isentropic- Neutral Solutes

Granted that $\phi\left(K_{\mathrm{Sj}};\ \mathrm{def}\ \right)$ has been measured for solutions containing neutral solutes (at defined T and p), interesting patterns emerge for the dependences of $\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)$ on molality m_j and on solute j. Further these dependences are readily extrapolated (geometrically) to infinite dilution to yield estimates of $\phi\left(K_{\mathrm{S}_j};\mathrm{def}\right)^{\infty}$. These comments apply to solutions of neutral solutes in both aqueous and non-aqueous solutions; e.g. solutions in propylene carbonate [1] and aqueous solutions of carbohydrates [2].

For dilute solutions of neutral solutes $\phi\left(K_{\mathrm{Sj}};\ \mathrm{def}\ \right)$ is often approximately a linear function of the molality m_j.

$$\text{Thus } \phi\left(\mathrm{K_{S_j}};\ \mathrm{def}\ \right)=\phi\left(\mathrm{K_{S_j}};\ \mathrm{def}\ \right)^{\infty}+\mathrm{b_{KS}}\ \left(\mathrm{m_j}/\mathrm{m}^0\right)$$

For aqueous solutions containing ureas, acetamides and α,ω-alkanediols, the slope b_{KS} is positive. For dextrose(aq), sucrose(aq), urea(aq) and thiourea(aq) φ(;) K def Sj ∞ is negative. In contrast φ(;) K def Sj ∞ is positive for dioxan(aq) and acetamide(aq). In other words $\phi\left(K_{\mathrm{S}_j};\mathrm{def}\right)^{\infty}$ is characteristic of the solute [3,4]. Group additivity schemes are discussed for $\phi\left(K_{\mathrm{S}_j};\mathrm{def}\right)^{\infty}$ with respect to glycylpeptides(aq) [5], amino acids(aq) [6-8] and alcohols [9-11]. With increase in temperature $\phi\left(K_{\mathrm{S}_j};\mathrm{def}\right)^{\infty}$ for amino acids(aq) [8] and glycyl dipeptides(aq) [12,13] increases. Particularly interesting in terms of solute-water interactions is the study reported by Galema et al [14, 15] who comment on the calculation of $\phi\left(K_{\mathrm{Sj}};\ \mathrm{def}\ \right)$ for solute-j using equation (b).

$$\mathrm{K_{sj}(aq;def)}=\phi\left(\mathrm{K_{sj}};\mathrm{def}\right)+\mathrm{m_j}\ \left[\partial\phi\left(\mathrm{K_{s}}j;\mathrm{def}\right)/\partial\mathrm{m_j}\right]_{\mathrm{T,p}}$$

This study confirmed the importance of the stereochemistry of carbohydrates on their hydration. A clear contrast is drawn between those solutes where the hydrophilic groups match and mismatch into the three dimensionally hydrogen - bonded structure of liquid water. With increase in solute concentration, the dependence of $\mathrm{K_{Sj}(aq;\ def}\ )$ on composition is non-linear [16]. For amines(aq) $\mathrm{K_{Sj}(aq;\ def}\ )$ passes through minima [16].

Chalikian discusses the isentropic compression of a wide range of solutes with reference to group contributions [17], the discussion being extended to proteins [18] and oligopeptides[19].

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1.7.7: Compressions- Isentropic- Salt Solutions

An extensive literature describes the isentropic compressibilities of salt solutions prompted by earlier studies by Passynski [1] described by Owen [2].

The isentropic compression of a given aqueous salt solution $\mathrm{K_s(aq)}$ is determined using the Newton-Laplace Equation in conjunction with speeds of sound and densities. An apparent molar compression of salt $j\phi\left(K_s;\ \mathrm{def}\ \right)$ is calculated using equation (a).

$$\mathrm{K_S\left(aq; w_1 = 1\ kg\right) = \left(1/M_1\right)\ K^*_{S1}}(\ell) + \mathrm{m_j}\,\phi\left(\mathrm{K_s; def}\right)$$

Here $\mathrm{K^*_{S1}}(\ell)$ is the isentropic compression of the solvent at the same T and p. For salt solutions, particularly aqueous salt solutions, the dependence of $\phi\left(\mathrm{K_{Sj};\ def}\ \right)$ on the molality of the salt is generally examined in the light of equations describing the role of ion-ion interactions [3; see also reference 4]. For dilute salt solutions, equation (b) forms the basis for examining the dependence of $\phi\left(\mathrm{K_{Sj};\ def}\ \right)$ on $\left(\mathrm{m_j}\right)^{1/2}$ where m_j is the molality of the salt-j.

$$\mathrm{Then,}\ \phi\left(\mathrm{K_{Sj};\ def}\ \right) = \phi\left(\mathrm{K_{Sj};\ def}\ \right)^{\infty} + \mathrm{S_{KS}}\ \left(\mathrm{m_j/m^0}\right)^{1/2}$$

The form of the equation (b) has all the hallmarks of a pattern required by the DHLL. In practice $\mathrm{S_{KS}}$ cannot be calculated because the required isentropic dependence of the relative permittivity of the solvent on pressure is generally not known. However a plot is obtained using equation (b) yielding an estimate of $\phi\left(\mathrm{K_{Sj}; def}\right)^{\infty}$.

For a large range of 1:1 salts $\phi\left(K_{S_j}; \mathrm{def}\right)^{\infty}$ is negative, a pattern attributed to electrostriction of neighbouring solvent molecules by electric charges on the ions [3-10]. $\phi\left(\mathrm{K_{S_j};\ def}\ \right)^{\infty}$ is more negative for solutions in $\mathrm{D_2O}$ than in $\mathrm{H_2O}$ as a consequence of more intense electrostriction in $\mathrm{D_2O}$ [5]. Further on the basis of the Desnoyers-Philip Equation, the difference $\phi\left(\mathrm{K_{Sj}; def}\right)^{\infty} - \phi\left(\mathrm{K_{T_j}}\right)^{\infty}$ is small but not negligible, amounting to approx. 10%. For alkylammonium ions in aqueous solutions $\phi\left(\mathrm{K_{Sj}; def}\right)^{\infty}$ decreases with increase in the hydrophobic character, matching a general increase in $\phi\left(V_j\right)^{\infty}$ [11]. Group and ionic contributions to $\phi\left(\mathrm{K_{Sj}; def}\right)^{\infty}$ have been estimated [10,11]. Indeed $\phi\left(\mathrm{K_{Sj};\ def}\ \right)$ is approximately a linear function of $\left(m_j/m^0\right)^{1/2}$ for a wide range of aqueous and non-aqueous salt solutions [11-13]; e.g. salts in DMSO [14] and in propylene carbonate [15]. $\phi\left(\mathrm{K_{Sj};\ def}\ \right)$ for copper(I) and sodium perchlorates in cyanobenzene, pyridine and cyanomethane show almost no dependence on salt molality [16].

A problem is further complicated by the fact that the DHLL for $\phi\left(K_{Sj};\ \mathrm{def}\ \right)$ is itself a complicated function of salt molality [17], $\mathrm{S_{KS}}\ \left(\mathrm{m_j/m^0}\right)^{1/2}$ being however the leading term. A problem is encountered with the differential dependence of the molar volume of the solvent $\mathrm{V^*_1}(\ell)$ on pressure at constant $\mathrm{S(s\,ln)}$ describing how the volume of the solution would depend on pressure if it were held at the same entropy of the solution. Thus [18]

$$\begin{aligned}-\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right]_{\mathrm{s(aq)}} &= \left[\kappa_{\mathrm{s}}(\mathrm{aq}) - \kappa^*_{\mathrm{s1}}(\ell)\right]\ \left[\mathrm{m_j}\,\rho^*_1(\ell)\right]^{-1} + \kappa_{\mathrm{s}}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)\\ &+ \left[\mathrm{m_j}\,\rho^*_1(\ell)\right]^{-1}\ \mathrm{T}\,\alpha^*_1(\ell)\ \left\{\left[\alpha_{\mathrm{p}}(\mathrm{aq})/\sigma(\mathrm{aq})\right] - \left[\alpha^*_{\mathrm{p1}}(\ell)/\sigma^*_1(\ell)\right]\right\}\end{aligned}$$

By definition,

$$\phi\left(\mathrm{K_{Sj}; def}\right) = \left[\kappa_{\mathrm{s}}(\mathrm{aq}) - \kappa^*_{\mathrm{S1}}(\ell)\right]\ \left[\mathrm{m_j}\,\rho^*_1(\ell)\right]^{-1} + \kappa_{\mathrm{s}}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$

Then,

$$\begin{aligned}-\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right]_{\mathrm{S(aq)}} &= \phi\left(\mathrm{K_{sj}; def}\right)\\ &+ \left[\mathrm{m_j}\,\rho^*_1(\ell)\right]^{-1}\ \mathrm{T}\,\alpha^*_1(\ell)\ \left\{\left[\alpha_{\mathrm{p}}(\mathrm{aq})/\sigma(\mathrm{aq})\right] - \left[\alpha^*_{\mathrm{p1}}(\ell)/\sigma^*_1(\ell)\right]\right\}\end{aligned}$$

Consequently the difference between $-\left[\frac{\partial\phi(\mathrm{V_j})}{\partial \mathrm{p}}\right]_{\mathrm{s(aq)}}$ and $\phi\left(\mathrm{K_{sj}; def}\right)$ is determined by the property $\Delta\phi$, defined in equation (f).

$$\Delta\phi = \left\{\left[\alpha_{\mathrm{p}}(\mathrm{aq})/\sigma(\mathrm{aq})\right] - \left[\alpha^*_{\mathrm{p1}}(\ell)/\sigma^*_1(\ell)\right]\right\}$$

However $\Delta\phi/\mathrm{m_j}$ is indeterminate at infinite dilution . But using L'Hospital's rule,

$$\mathrm{Limit}\ \left(\mathrm{m_j} \to 0\right)\Delta\phi/\mathrm{m_j} = \left[\left[\rho^*_1(\ell)\,\alpha^*_{p1}(\ell)/\sigma^*_1(\ell)\right]\ \left\{\frac{\phi\left(E_{pj}\right)^{\infty}}{\alpha^*_{p1}(\ell)}\right] - \left[\frac{\phi\left(C_{pj}\right)^{\infty}}{\sigma^*_1(\ell)}\right]\right\}$$

Despite the thermodynamic polish given to the analysis of isentropic compressions, the problem of contrasting conditions ‘at constant $\mathrm{S(aq)}$’ and ‘at constant $\mathrm{S_1^*(\ell)}$’ underlies the analysis.

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1.7.8: Compresssions- Isentropic- Aqueous Solution

A given aqueous solution is prepared using n_1 moles of water and n_j moles of solute j. The thermodynamic properties of this solution are ideal.

$$\text{Then,} \quad V_m(aq;\ \mathrm{id}\ ) = x_1\, V_1^*(\ell) + x_j\, \phi\,(V_j)^\infty$$

$$\text{Here } \phi\,(\mathrm{V_j})^\infty = \mathrm{V_j^\infty(aq)} = \text{limit}\,(\mathrm{n_j} \rightarrow 0)\left(\frac{\partial \mathrm{V(aq;id)}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(1)}}$$

The molar entropy of the ideal solution is given by equation (c).

$$\mathrm{S_m(aq;id) = x_1\, S_1^*(\ell) - x_1\, R\, \ln(x_1) + x_j\, S_j(aq;id)}$$

$\mathrm{S_j(aq;id)}$ is the partial molar entropy of solute j at the same T and p. The solution is perturbed by a change in pressure and displaced to a neighbouring state having the same entropy, $\mathrm{S_m(aq;id)}$.

$$\mathrm{K_{Sm}(aq;id) = -\left(\frac{\partial V_m(aq;id)}{\partial p}\right)_{S(m;aq;jd),x(j)}}$$

From equation (a),

$$\mathrm{K_{Sm(a;;dd)} = -x_1\left(\frac{\partial V_1^*(\ell)}{\partial p}\right)_{S(m;aq;id),x(j)} - x_j\left(\frac{\partial \phi\,(V_j)^\infty}{\partial p}\right)_{S(m;aq;;dd),x(j)}}$$

On these partial differentials, the isentropic condition is not the most convenient because it refers to the entropy of an ideal solution. Using the technique adopted for liquid mixtures, we obtain in equation (f), an expression for the unconventional isentropic compression of the solvent .

$$\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(m;aq;dd),x(j)}} =$$
$$\mathrm{-K_{S1}^*}(\ell) - \mathrm{T}\ \left[\mathrm{E_{p1}^*}(\ell)\right]^2/\mathrm{C_{p1}^*}(\ell) + \mathrm{T\,E_{p1}^*}(\ell)\,\mathrm{E_{pm}(aq;id)/C_{pm}(aq;id)}$$

Or,

$$\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(m;qq;id),x(j)}} =$$
$$\mathrm{-K_{S1}^*}(\ell) - \mathrm{T\,E_{p1}^*}(\ell)\ \left[\mathrm{E_{p1}^*}(\ell)/\mathrm{C_{p1}^*}(\ell) - \mathrm{E_{pm}(aq;id)/C_{pm}(aq;id)}\right]$$

Except for the different ideal reference state, equation (g) for the solvent is formally identical to the corresponding equation for liquid mixtures. However, in this case we need to follow a different approach for chemical substance j. The appropriate choice for isentropic conditions on solute properties is the entropy of the pure solvent at same T and p. Hence,

$$\left(\frac{\partial \phi\,(\mathrm{V_j})^\infty}{\partial \mathrm{p}}\right)_{\mathrm{s(m;aq;id),x(j)}} =$$

Or,

$$\left(\frac{\partial \phi\,(\mathrm{V_j})^\infty}{\partial \mathrm{p}}\right)_{\mathrm{S(m;aq;id),x(j)}} = \left(\frac{\partial \phi\,(\mathrm{V_j})^\infty}{\partial \mathrm{p}}\right)_{\mathrm{s_1^*}(\ell)}$$
$$-\mathrm{T}\,\phi\,(\mathrm{E_{pj}})^\infty\,\frac{\mathrm{E_{p1}^*}(\ell)}{\mathrm{C_{pl}^*}(\ell)} + \mathrm{T}\,\phi\,(\mathrm{E_{pj}})^\infty\,\frac{\mathrm{E_{pm}(aq;id)}}{\mathrm{C_{pm}(aq;id)}}$$

Or,

$$\left(\frac{\partial \phi\,(\mathrm{V_j})^\infty}{\partial \mathrm{p}}\right)_{\mathrm{S(m;aq;id),\times(j)}} = \left(\frac{\partial \phi\,(\mathrm{V_j})^\infty}{\partial \mathrm{p}}\right)_{\mathrm{s_1^*}(\ell)}$$
$$-\mathrm{T}\,\phi\,(\mathrm{E_{pj}})^\infty\,\left[\frac{\mathrm{E_{p1}^*}(\ell)}{\mathrm{C_{p1}^*}(\ell)} - \frac{\mathrm{E_{pm}(aq;id)}}{\mathrm{C_{pm}(aq;id)}}\right]$$

The isentropic pressure dependences of apparent and partial molar volumes are complicated functions. We are interested in obtaining an expression for $\mathrm{K_{Sm}(aq;id)}$ in terms of the limiting apparent or partial molar isentropic compression of solute j, $\phi\left(\mathrm{K_{Sj}}\right)^{\infty}$. We use the following expression [1-3].

$$\left(\frac{\partial \phi\left(\mathrm{V_j}\right)^{\infty}}{\partial \mathrm{p}}\right)_{\mathrm{s_i^*}(\ell)} = -\phi\left(\mathrm{K_{Sj}}\right)^{\infty} - \mathrm{T}\left(\frac{\left[\mathrm{E_{p1}^*}(\ell)\right]^2}{\mathrm{C_{p1}^*}(\ell)}\right)\left(\frac{\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\mathrm{E_{p1}^*}(\ell)} - \frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\mathrm{C_{p1}^*}(\ell)}\right)$$

We combine the results in equations (e), (g), (j) and (k) to obtain an equation for $\mathrm{K_{Sm}(aq;id)}$; equation (l).

$$\begin{aligned}
&\mathrm{K_{Sm}(aq;id)} = \\
&\mathrm{x_1\,K_{s1}^*}(\ell) + \mathrm{x_1\,T\,E_{p1}^*}(\ell)\left[\frac{\mathrm{E_{pl}^*}(\ell)}{\mathrm{C_{p1}^*}(\ell)} - \frac{\mathrm{E_{pm}(aq;id)}}{\mathrm{C_{pm}(aq;id)}}\right] \\
&+ \mathrm{x_j}\,\phi\left(\mathrm{K_{sj}}\right)^{\infty} + \mathrm{x_j\,T}\left[\frac{\left[\mathrm{E_{pl}^*}(\ell)\right]^2}{\mathrm{C_{pl}^*}(\ell)}\right]\left[\frac{\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\mathrm{E_{p1}^*}(\ell)} - \frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\mathrm{C_{p1}^*}(\ell)}\right] \\
&+ \mathrm{x_j\,T}\,\phi\left(\mathrm{E_{pj}}\right)^{\infty}\left[\frac{\mathrm{E_{p1}^*}(\ell)}{\mathrm{C_{p1}^*}(\ell)} - \frac{\mathrm{E_{pm}(aq;id)}}{\mathrm{C_{pm}(aq;id)}}\right]
\end{aligned}$$

Finally, by noting that $\mathrm{E_{pm}(aq;id)} = \mathrm{x_1\,E_{p1}^*}(\ell) + \mathrm{x_j}\,\phi\left(\mathrm{E_{pj}}\right)^{\infty}$ after slight simplification we arrive at an expression for $\mathrm{K_{Sm}(aq;1\ d)}$; equation (m).

$$\begin{aligned}
&\mathrm{K_{Sm}(aq;id)} = \mathrm{x_1}\left\{\mathrm{K_{s1}^*}(\ell) + \mathrm{T}\left[\mathrm{E_{p1}^*}(\ell)\right]^2/\mathrm{C_{p1}^*}(\ell)\right\} \\
&+ \mathrm{x_j}\left\{\phi\left(\mathrm{K_{Sj}}\right)^{\infty} + \mathrm{T}\left(\frac{\left[\mathrm{E_{pl}^*}(\ell)\right]^2}{\mathrm{C_{p1}^*}(\ell)}\right)\left(\frac{2\,\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\mathrm{E_{pl1}^*}(\ell)} - \frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\mathrm{C_{pl1}^*}(\ell)}\right)\right. \\
&\left. - \mathrm{T}\,\frac{\left[\mathrm{E_{pm}(aq;id)}\right]^2}{\mathrm{C_{pm}(aq;id)}}\right.
\end{aligned}$$

The complexity of equation (m) for solutions can be attributed to a combination of the non-Gibbsian character of $\mathrm{K_{Sm}(aq;1\ d)}$ with the non-Lewisian character of $\phi\left(\mathrm{K_{Sj}}\right)^{\infty}$. Clearly $\mathrm{K_{Sm}(aq;1\ d)}$ and $\mathrm{K_{mix}(aq;1\ d)}$ are not equal because the reference states for chemical substance j differ. We are interested in the apparent molar isentropic compression of solute j in ideal aqueous solutions $\phi\left(\mathrm{K_{Sj}}\right)\mathrm{(aq;id)}$, which is defined in equation (n) and expressed by equation (o).

$$\mathrm{K_{Sm}(aq;id)} = \mathrm{x_1\,K_{SI}^*}(\ell) + \mathrm{x_j}\,\phi\left(\mathrm{K_{Sj}}\right)\mathrm{(aq;id)}$$

$$\begin{aligned}
&\phi\left(\mathrm{K_{sj}}\right)\mathrm{(aq;id)} = \phi\left(\mathrm{K_{Sj}}\right)^{\infty} \\
&+ \mathrm{T}\left(\frac{\left[\mathrm{E_{pl1}^*}(\ell)\right]^2}{\mathrm{C_{p1}^*}(\ell)}\right)\left[\frac{2\,\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\mathrm{E_{p1}^*}(\ell)} - \frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\mathrm{C_{p1}^*}(\ell)}\right] \\
&+ \mathrm{T}\left(\frac{\mathrm{x_1}\left[\mathrm{E_{pl}^*}(\ell)\right]^2}{\mathrm{C_{pl1}^*}(\ell)} - \frac{\left[\mathrm{E_{pm}(aq;id)}\right]^2}{\mathrm{C_{pm}(aq;id)}}\right)\frac{1}{\mathrm{x_j}}
\end{aligned}$$

Limiting values for $\phi\left(\mathrm{K_{Sj}}\right)\mathrm{(aq;id)}$ are interesting. For the ideal solution at $\mathrm{x}_j = 0$, which is the same state as the real solution at infinite dilution, we naturally obtain $\phi\left(\mathrm{K_{S_j}}\right)^{\infty}$ although using equation (o) for this purpose requires solving an indeterminate form. For the ideal solution at $\mathrm{x}_j = 0$ we obtain equation (p), which yields equation (q) after major reorganisation.

$$\begin{aligned}
&\mathrm{limit}\,(\mathrm{x_j} \to 1)\,\phi\left(\mathrm{K_{sj}}\right)\mathrm{(aq;id)} = \phi\left(\mathrm{K_{s}}j\right)^{\infty} \\
&+ \mathrm{T}\left(\frac{\left[\mathrm{E_{pl}^*}(\ell)\right]^2}{\mathrm{C_{p1}^*}(\ell)}\right)\left[\frac{2\,\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\mathrm{E_{p1}^*}(\ell)} - \frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\mathrm{C_{p1}^*}(\ell)}\right] - \mathrm{T}\left(\frac{\left[\phi\left(\mathrm{E_{pj}}\right)^{\infty}\right]^2}{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}\right)
\end{aligned}$$

$$\begin{aligned}
&\mathrm{limit}\,(\mathrm{x_j} \to 1)\,\phi\left(\mathrm{K_{s}}j\right)\mathrm{(aq;id)} = \phi\left(\mathrm{K_{sj}}\right)^{\infty} \\
&- \mathrm{T}\left(\frac{\left[\mathrm{E_{p1}^*}(\ell)\right]^2}{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}\right)\left[\frac{\phi\left(\mathrm{E_{p}}j\right)^{\infty}}{\mathrm{E_{p1}^*}(\ell)} - \frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\mathrm{C_{p1}^*}(\ell)}\right]
\end{aligned}$$

The latter equation expresses the molar isentropic compression of solute j in a standard state of unit mole fraction in terms of properties for the pure solvent and for the solute at infinite dilution. The ideal aqueous solution may be described as a non-ideal

liquid mixture. An excess property is defined by equation (r).

$$\phi\left(\mathrm{K_{Sj}}\right)^{\mathrm{E}} = \phi\left(\mathrm{K_{Sj}}\right)(\mathrm{aq;id}) - \phi\left(\mathrm{K_{Sj}}\right)(\ \mathrm{mix;id})$$

$$\text{Or, } \phi\left(K_{Sj}\right)^{E} = \left[K_{Sm}(\mathrm{aq};id) - K_{Sm}(\mathrm{mix};i\ \mathrm{d})\right]/x_j$$

A working equation for $\phi\left(\mathrm{K_{Sj}}\right)^{\mathrm{E}}$ can be generated from equation (o). After little reorganisation, we obtain equation (t).

$$\begin{aligned}\phi\left(\mathrm{K_{Sj}}\right)^{\mathrm{E}} &= \phi\left(\mathrm{K_{Sj}}\right)^{\infty} - \mathrm{K^{*}_{Sj}}(\ell)\\ &+ \mathrm{T}\left[\frac{\left[\mathrm{E^{*}_{p1}}(\ell)\right]^{2}}{\mathrm{C^{*}_{p1}}(\ell)}\right]\left[\frac{2\,\phi\left(\mathrm{E^{\infty}_{pj}}\right)}{\mathrm{E^{*}_{pl1}}(\ell)} - \frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\mathrm{C^{*}_{p1}}(\ell)}\right] - \mathrm{T}\,\frac{\left[\mathrm{E^{*}_{p1}}(\ell)\right]^{2}}{\mathrm{C^{*}_{p1}}(\ell)}\\ &- \mathrm{T}\left[\frac{\left[\mathrm{E_{pm}(aq;id)}\right]^{2}}{\mathrm{C_{pm}(aq;id)}} - \frac{\left[\mathrm{E_{pm}(mix;id)}\right]^{2}}{\mathrm{C_{pm}(mix;id)}}\right]\frac{1}{\mathrm{x_j}}\end{aligned}$$

Interestingly, the first four terms on the right end side of equation (t) express the difference $\phi\left(\mathrm{K_{T_j}}\right)^{\infty} - \mathrm{K^{*}_{T_j}}(\ell)$. For solution chemists the important reference state is at infinite dilution. The limiting excess property $\phi\left(\mathrm{K_{Sj}}\right)^{\mathrm{E},\infty}$ is given by equation (u) [4].

$$\begin{aligned}\phi\left(\mathrm{K_{Sj}}\right)^{\mathrm{E},\infty} &= \phi\left(\mathrm{K_{Sj}}\right)^{\infty} - \mathrm{K^{*}_{S1}}(\ell)\\ &- \mathrm{T\,C^{*}_{p1}}(\ell)\left[\frac{\mathrm{E^{*}_{pj}}(\ell)}{\mathrm{C^{*}_{p}}_{j}(\ell)} - \frac{\mathrm{E^{*}_{p1}}(\ell)}{\mathrm{C^{*}_{p1}}(\ell)}\right]^{2}\end{aligned}$$

Estimates of $\phi\left(\mathrm{K_{Sj}}\right)^{\infty}$ using $\phi\left(\mathrm{K_{Sj}}\right)^{\mathrm{E},\infty}$ data for binary liquid mixtures often neglect the last term in equation (u).

Equation (u) works in two ways. A solution chemist will estimate $\phi\left(K_{Sj}\right)^{\infty}$ from data reporting $\phi\left(K_{\mathrm{Sj}}\right)^{\mathrm{E},\infty}$. A chemist interested in the properties of liquid mixtures will estimate $\phi\left(K_{\mathrm{Sj}}\right)^{\mathrm{E},\infty}$ from data reporting $\phi\left(K_{Sj}\right)^{\infty}$.

Footnotes

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1.7.9: Compressions- Isentropic and Isothermal- Solutions- Approximate Limiting Estimates

The Newton Laplace Equation relates the speed of sound u in an aqueous solution, density $\rho(\mathrm{aq})$ and isentropic compressibility $\kappa_{\mathrm{S}}(\mathrm{aq})$; equation (a).

$$\mathrm{u}^2 = [\kappa_{\mathrm{s}}(\mathrm{aq})\,\rho(\mathrm{aq})]^{-1}$$

The differential dependence of sound velocity u on $\kappa_{\mathrm{S}}(\mathrm{aq})$ and $\rho(\mathrm{aq})$ is given by equation (b).

$$2\,u(aq)\,du(aq) = -\frac{1}{[\kappa_{\mathrm{s}}(aq)]^2\;\rho(aq)}\,d\kappa_s(aq) - \frac{1}{\kappa_s(aq)]\;[\rho(aq)]^2}\,d\rho(aq)$$

We divide equation (b) by equation (a).

$$2\,\frac{\mathrm{du(aq)}}{\mathrm{u(aq)}} = -\frac{\mathrm{d}\kappa_{\mathrm{s}}(\mathrm{aq})}{\kappa_{\mathrm{s}}(\mathrm{aq})} - \frac{\mathrm{d}\rho(\mathrm{aq})}{\rho(\mathrm{aq})}$$

We explore three approaches based on equation (c)

Analysis I

Two extra-thermodynamic assumptions are made.

i. Sound velocity $\mathrm{u(aq)}$ is a linear function of solute concentration, c_j.

$$\text{Thus[1]} \quad \mathrm{u(aq)} = \mathrm{u}_1^*(\ell) + \mathrm{A_u\,c_j}$$

$$\text{By definition,} \quad \mathrm{du(aq)} = \mathrm{u(aq)} - \mathrm{u}_1^*(\ell) = \mathrm{A_u\,c_j}$$

ii. Density $\rho(\mathrm{aq})$ is a linear function of concentration c_j.

$$\text{Thus[1]} \quad \rho(\mathrm{aq}) = \rho_1^*(\ell) + \mathrm{A}_\rho\,\mathrm{c_j}$$

$$2\,\frac{\mathrm{A_u\,c_j}}{\mathrm{u(aq)}} = -\frac{\mathrm{d}\kappa_{\mathrm{S}}(\mathrm{aq})}{\mathrm{K_s(aq)}} - \frac{\mathrm{A}_\rho\,\mathrm{c_j}}{\rho(\mathrm{aq})}$$

$$\frac{\mathrm{d}\kappa_{\mathrm{S}}(\mathrm{aq})}{\kappa_{\mathrm{S}}(\mathrm{aq})} = -2\,\frac{\mathrm{A_u\,c_j}}{\mathrm{u(aq)}} - \frac{\mathrm{A}_\rho\,\mathrm{c_j}}{\rho(\mathrm{aq})}$$

In principle the change in $\kappa_{\mathrm{S}}(\mathrm{aq})$ resulting from addition of a solute j to form a solution concentration c_j can be obtained from the experimentally determined parameters A_ρ and $\mathrm{A_u}$.

Analysis II

Another approach expresses the two dependences using a general polynomial in c_j.

$$\text{By definition,} \quad \mathrm{A_u^\infty} = \mathrm{limit}\,(\mathrm{c_j} \to 0)\left(\frac{\partial \mathrm{u(aq)}}{\partial \mathrm{c_j}}\right)_{\mathrm{T,p}}$$

$$\text{and } \mathrm{A}_\rho^\infty = \mathrm{limit}\,(\mathrm{c_j} \to 0)\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{c_j}}\right)_{\mathrm{T,p}}$$

The assumption is made that both $\mathrm{A_u^\infty}$ and A_ρ^∞ are finite.

$$\text{Similarly } \mathrm{limit}\,(\mathrm{c_j} \to 0)\left(\frac{\kappa_{\mathrm{s}}(\mathrm{aq}) - \kappa_{\mathrm{S}}^*(\ell)}{\mathrm{c_j}}\right)_{\mathrm{T,p}} = \left(\frac{\partial \kappa_{\mathrm{S}}(\mathrm{aq})}{\partial \mathrm{c_j}}\right)_{\mathrm{T,p}}^{\infty}$$

Analysis III

The procedures described above are incorporated into the following equation for $\phi\,(\mathrm{K_{sj}; def})$.

$$\text{Thus } \phi\left(\mathrm{K_{sj}};\ \text{def}\right) = \left[\mathrm{c_j}\right]^{-1}\left[\kappa_\mathrm{s}(\mathrm{aq}) - \kappa^*_{\mathrm{s1}}(\ell)\right] + \phi\left(\mathrm{V_j}\right)\ \kappa^*_{\mathrm{s1}}(\ell)$$

Hence using equation (h) with $\mathrm{d_s(aq)} = \kappa_\mathrm{s}(\mathrm{aq}) - \kappa^*_{\mathrm{s1}}(\ell)$

$$\phi\left(\mathrm{K_{Sj}};\ \text{def}\right) = \left[\kappa_\mathrm{S}(\mathrm{aq})/\mathrm{c_j}\right]\left[-\frac{2\,\mathrm{A_u\,c_j}}{\mathrm{u(aq)}} - \frac{\mathrm{A}_\rho\,\mathrm{c_j}}{\rho(\mathrm{aq})}\right] + \phi\left(\mathrm{V_j}\right)\ \mathrm{K^*_{S1}}(\ell)$$

If we assume that $\kappa_\mathrm{S}(\mathrm{aq})$ is close to $\kappa^*_{\mathrm{S1}}(\ell)$, then [2]

$$\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right) = \kappa_\mathrm{s}(\mathrm{aq})\left[-\frac{2\,\mathrm{A_u}}{\mathrm{u(aq)}} - \frac{\mathrm{A}_\rho}{\rho(\mathrm{aq})} + \phi\left(\mathrm{V_j}\right)\right]$$

Equation (n) is complicated in the sense that the properties $\kappa_\mathrm{S}(\mathrm{aq})$, $\mathrm{u(aq)}$, $\rho(\mathrm{aq})$ and $\phi\left(\mathrm{V_j}\right)$ depend on concentration c_j. With respect to $\phi\left(\mathrm{V_j}\right)$, the following equation is exact.

$$\phi\left(\mathrm{V_j}\right) = \left[\mathrm{c_j}\,\rho^*_1(\ell)\right]^{-1}\left[\rho^*_1(\ell) - \rho(\mathrm{aq})\right] + \mathrm{M_j}/\rho^*_1(\ell)$$

$$\text{Using equation } (f), \phi\left(V_j\right) = -\frac{A_\rho}{\rho^*_1(\ell)} + \frac{M_j}{\rho^*_1(\ell)}$$

$$\text{Or, } -\frac{A_\rho}{\rho^*_1(\ell)} = \phi\left(V_j\right) - \frac{M_j}{\rho^*_1(\ell)}$$

Equation (q) is multiplied by the ratio, $\rho^*_1(\ell)/\rho(\mathrm{aq})$.

$$\text{Thus } -\frac{\mathrm{A}_\rho}{\rho(\mathrm{aq})} = \frac{\rho^*_1(\ell)}{\rho(\mathrm{aq})}\,\phi\left(\mathrm{V_j}\right) - \frac{\mathrm{M_j}}{\rho(\mathrm{aq})}$$

Combination of equations (n) and (r) yields equation (s).

$$\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right) = \kappa_\mathrm{s}\left[-\frac{2\,\mathrm{A_u}}{\mathrm{u(aq)}} + \frac{\rho^*_1(\ell)}{\rho(\mathrm{aq})}\,\phi\left(\mathrm{V_j}\right) - \frac{\mathrm{M_j}}{\rho(\mathrm{aq})} + \phi\left(\mathrm{V_j}\right)\right]$$

The argument is advanced that $\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)$ can be meaningfully extrapolated to infinite dilution.

$$\text{limit}\,(c_j \to 0)\,\phi\left(K_{\mathrm{Sj}_j};\mathrm{def}\right) = \phi\left(\mathrm{K_{sj}};\mathrm{def}\right)^\infty$$

In the same limit $\rho^*_1(\ell)/\rho(\mathrm{aq}) = 1.0$ and $\mathrm{K_S(aq)} = \mathrm{K^*_S}(\ell)$.

$$\phi\left(\mathrm{K_{S_j}};\mathrm{def}\right)^\infty = \kappa^*_{\mathrm{s1}}(\ell)\left[2\,\phi\left(\mathrm{V_j}\right)^\infty - \frac{\mathrm{M_j}}{\rho^*_1(\ell)} - \frac{2\,\mathrm{A_u}}{\mathrm{u}^*_1(\ell)}\right]$$

$$\text{But from equation (d)}, \mathrm{A_u} = \left[\mathrm{u(aq)} - \mathrm{u}^*_1(\ell)\right]/\mathrm{c_j}$$

$$\phi\left(\mathrm{K_{sj}};\mathrm{def}\right)^\infty = \kappa^*_{\mathrm{sl}}(\ell)\left[2\,\phi\left(\mathrm{V_j}\right)^\infty - 2\,\mathrm{U} - \frac{\mathrm{M_j}}{\rho^*_1(\ell)}\right]$$

where (cf. equation (v)),

$$\mathrm{U} = \left[\mathrm{u(aq)} - \mathrm{u}^*_1(\ell)\right]/\left[\mathrm{u}^*_1(\ell)\,\mathrm{c_j}\right]$$

The symbol U identifies the relative molar increment of the speed of sound [3-9]. Equation (w) shows $\phi\left(K_{S_j};\mathrm{def}\right)^\infty$ is obtained from $\phi\left(\mathrm{V_j}\right)^\infty$ and the speed of sound in a solution concentration c_j.

$$\text{In this approach we assume that } \left(\frac{\partial \mathrm{u}}{\partial \mathrm{c_j}}\right)_{\mathrm{T,p}} = \frac{\mathrm{u(aq)} - \mathrm{u}^*_1(\ell)}{\mathrm{c_j}}$$

$$\text{Then, } U = \frac{1}{\mathrm{u}^*_1(\ell)}\left(\frac{\mathrm{du(aq)}}{\mathrm{dc_j}}\right)$$

However $\left(\frac{\mathrm{du(aq)}}{\mathrm{dc}}\right)$ and similarly $\left(\frac{\mathrm{du(aq)}}{\mathrm{dm_j}}\right)$ are obtained using experimental results for real concentrations. Hence the estimated $\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^\infty$ is likely to be poor.

Analysis IV

The apparent molar isothermal compression of solute j is related to the concentration c_j using the following exact equation.

$$\phi\left(K_{T_j}\right) = [c_j]^{-1}\left[\kappa_T(aq) - \kappa^*_{T1}(\ell)\right] + \phi\left(V_j\right)\,\kappa^*_{T1}(\ell)$$

$$\text{By definition.} \quad \delta(aq) = \kappa_T(aq) - \kappa_S(aq)$$

$$\text{and } \delta^*_1(1) = \kappa^*_{T1}(\ell) - \kappa^*_{S1}(\ell)$$

$$\text{For an aqueous solution, } \kappa_T(aq) = \delta(aq) + \kappa_s(aq)$$

According to the Newton-Laplace Equation.

$$[u(aq)]^2 = [\kappa_s(aq)\,\rho(aq)]^{-1}$$

$$\text{From equation (zd)}, \kappa_T(aq) = \delta(aq) + \left\{[u(aq)]^2\,\rho(aq)\right\}^{-1}$$

At this stage, assumptions are made concerning the dependences of $\kappa_T(aq)$ and $\delta(aq)$ on concentration c_j.

$$\text{Thus} \quad \kappa_T(aq) = \kappa^*_{T1}(\ell) + A_{KT}\,c_j$$

$$\text{and} \quad \delta(aq) = \delta^*_1(\ell) + A_\delta\,c_j$$

Using equations (d), (f) and (zf),

$$\kappa^*_{Tl}(\ell) + A_{\kappa T}\,c_j = \delta^*_1(\ell) + A_\delta\,c_j + \frac{1}{\left\{u^*_1(\ell) + A_u\,c_j\right\}^2\left\{\rho^*_1(\ell) + A_\rho\,c_j\right\}}$$

Or,

$$\kappa^*_{T1}(\ell) + A_{\kappa T}\,c_j = \delta^*_1(\ell) + A_\delta\,c_j + \frac{1}{[u^*_1(\ell)]^2\left\{1 + A_u\,c_j/u^*_1(\ell)\right\}^2\rho^*_1(\ell)\left\{1 + A_\rho\,c_j/\rho^*_1(\ell)\right\}}$$

Assuming $A_u\,c_j/u^*_1(\ell) << 1$ and $A_\rho\,c_j/\rho^*_1(\ell) << 1$,

$$\kappa^*_{T1}(\ell) + A_{KT}\,c_j = \delta^*_1(\ell) + A_\delta\,c_j + \frac{1}{[u^*_1(\ell)]^2\,\rho^*_1(\ell)}\left[1 - \frac{2\,A_u\,c_j}{u^*_1(\ell)}\right]\left[1 - \frac{A_\rho\,c_j}{\rho^*_1(\ell)}\right]$$

$$\text{We assume that } \left[\frac{2\,A_u\,c_j}{u^*_1(\ell)}\right]\left[\frac{A_\rho\,c_j}{\rho^*_1(\ell)}\right] << 1$$

Therefore,

$$\kappa^*_{T1}(\ell) + A_{KT}\,c_j = \delta^*_1(\ell) + A_\delta\,c_j + \frac{1}{[u^*_1(\ell)]^2\,\rho^*_1(\ell)}\left[1 - \frac{2\,A_u\,c_j}{u^*_1(\ell)} - \frac{A_\rho\,c_j}{\rho^*_1(\ell)}\right]$$

$$\text{But } \kappa^*_{s1}(\ell) = \left\{[u^*_1(\ell)]^2\,\rho^*_1(\ell)\right\}^{-1}$$

$$\text{and } \kappa^*_{T1}(\ell) = \delta^*_1(\ell) + \kappa^*_{S1}(\ell)$$

Then,

$$\delta^*_1(\ell) + \kappa^*_{S1}(\ell) + A_{KT}\,c_j = \delta^*_1(\ell) + A_\delta\,c_j + \kappa^*_{Sl}(\ell)\left[1 - \frac{2\,A_u\,c_j}{u^*_1(\ell)} - \frac{A_\rho\,c_j}{\rho^*_1(\ell)}\right]$$

$$\text{Or } A_K = A_\delta - \kappa^*_{S1}(\ell)\left[\frac{2\,A_u}{u^*_1(\ell)} + \frac{A_\rho}{\rho^*_1(\ell)}\right]$$

From equations (za) and (zg),

$$\phi\left(\mathrm{K_{T_j}}\right) = \mathrm{A_{KT}} + \phi\left(\mathrm{V_j}\right)\ \kappa^*_{\mathrm{Tl}}(\ell)$$

Equations (zq) and (zr) yield equation (as),

$$\phi\left(\mathrm{K_{T_j}}\right) = \mathrm{A}_\delta - \kappa^*_{\mathrm{S1}}(\ell)\ \left[\frac{2\,\mathrm{A_u}}{\mathrm{u}^*_1(\ell)} + \frac{\mathrm{A}_\rho}{\rho^*_1(\ell)}\right] + \phi\left(\mathrm{V_j}\right)\ \kappa^*_{\mathrm{T1}}(\ell)$$

Or, using equation (q)

$$\phi\left(\mathrm{K_{T_j}}\right) = \mathrm{A}_\delta - \mathrm{K}^*_{\mathrm{S1}}(\ell)\,[\,\frac{2\,\mathrm{A_u}}{\mathrm{u}^*_1(\ell)} + \frac{\mathrm{M_j}}{\rho^*_1(\ell)} - \phi\left(\mathrm{V_j}\right)\Big] + \phi\left(\mathrm{V_j}\right)\ \kappa^*_{\mathrm{T1}}(\ell)$$

Using equation (zc),

$$\phi\left(\mathrm{K_{T_{j_j}}}\right) = \mathrm{A}_\delta - \kappa^*_{\mathrm{S1}}(\ell)\ \left[\frac{2\,\mathrm{A_u}}{\mathrm{u}^*_1(\ell)} + \frac{\mathrm{M_j}}{\rho^*_1(\ell)} - \phi\left(\mathrm{V_j}\right)\right] + \phi\left(\mathrm{V_j}\right)\ \delta^*_1(\ell) + \phi\left(\mathrm{V_j}\right)\ \kappa^*_{\mathrm{S1}}(\ell)$$

Or,

$$\phi\left(\mathrm{K_{T_j}}\right) = \mathrm{A}_\delta + \phi\left(\mathrm{V_j}\right)\ \delta^*_1(\ell) + \kappa^*_{\mathrm{Sl}}(\ell)\ \left[2\,\phi\left(\mathrm{V_j}\right) - \frac{\mathrm{M_j}}{\rho^*_1\ell)} - \frac{2\,\mathrm{A}_u}{\mathrm{u}^*_1\ell)}\right]$$

The latter is the Owen-Simons Equation[4] which takes the following form in the limit of infinite dilution.

$$\phi\left(\mathrm{K_{T_j}}\right)^\infty = [\mathrm{A}_\delta + \phi\left(\mathrm{V_j}\right)^\infty\ \delta^*_1(\ell)] + \kappa^*_{\mathrm{Sl}}(\ell)\ \left[2\,\phi\left(\mathrm{V_j}\right)^\infty - \frac{\mathrm{M_j}}{\rho^*_1(\ell)} - \frac{2\,\mathrm{A_u}}{\mathrm{u}^*_1(\ell)}\right]$$

The term $[\mathrm{A}_\delta + \phi\left(\mathrm{V_j}\right)^\infty\ \delta^*_1(\ell)]$ is not negligibly small. Using equation (u), equation (zw) takes the following form,

$$\phi\left(\mathrm{K_{T_j}}\right)^\infty = [\mathrm{A}_\delta + \phi\left(\mathrm{V_j}\right)^\infty\ \delta^*_1(\ell)] + \phi\left(\mathrm{K_{Sj}}\right)^\infty$$

Clearly the approximation which sets $\phi\left(\mathrm{K_{Tj}}\right)^\infty$ equal to $\phi\left(\mathrm{K_{Sj}}\right)^\infty$ is poor although often made. In fact Hedwig and Hoiland [10] show that for N-acetylamino acids in aqueous solution at 298.15 K$\phi\left(\mathrm{K_{T_j}}\right)^\infty$ and $\phi\left(\mathrm{K_{Sj}}\right)^\infty$ can have different signs, offering convincing evidence that the assumption is untenable.

Footnotes

[1]
$$A_u = \left[\frac{m}{s}\right]\ \left[\frac{m^3}{mol}\right] = \left[m^4\ \mathrm{s}^{-1}\ \mathrm{mol}^{-1}\right]$$
$$A_\rho = \left[\frac{kg}{m^3}\right]\ \left[\frac{m^3}{mol}\right] = \left[kg\ \mathrm{mol}^{-1}\right]$$

$$2\,\frac{\mathrm{A_u}}{\mathrm{u}}\,\mathrm{K_S(aq)} = [1]\ \frac{1}{[\ \mathrm{m\ s}^{-1}]}\ \left[\mathrm{m}^4\ \mathrm{s}^{-1}\ \mathrm{mol}^{-1}\right]\ \frac{1}{[\ \mathrm{N\ m}^{-2}]} = \frac{\left[\mathrm{m}^3\ \mathrm{mol}^{-1}\right]}{[\mathrm{Nm}^{-2}]}$$

[2]
$$\frac{\mathrm{A}_\rho}{\rho}\,\kappa_{\mathrm{S}}(\mathrm{aq}) = \frac{[\mathrm{kgm}^{-3}]}{[\mathrm{molm}^{-3}]}\ \frac{1}{\mathrm{kg\ m}^{-3}]}\ \frac{1}{[\ \mathrm{N\ m}^{-2}]} = \frac{\left[\mathrm{m}^3\ \mathrm{mol}^{-1}\right]}{[\mathrm{Nm}^{-2}]}$$

$$\phi\left(\mathrm{V_j}\right)\ \kappa_{\mathrm{s}}(\mathrm{aq}) = \left[\mathrm{m}^3\ \mathrm{mol}^{-1}\right]\ \frac{1}{[\ \mathrm{N\ m}^{-2}]} = \frac{\left[\mathrm{m}^3\ \mathrm{mol}^{-1}\right]}{[\mathrm{Nm}^{-2}]}$$

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1.7.10: Compressions- Desnoyers - Philip Equation

In terms of isentropic and isothermal compressibilities the Desnoyers-Philip Equation is important. A key equation expresses the difference between two apparent properties, $\phi\left(\mathrm{K_{T_j}}\right)^{\infty}$ and $\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^{\infty}$ [1]. We develop the proof in the general case starting from equation (a).

$$\delta = \kappa_{\mathrm{T}} - \kappa_{\mathrm{S}} = \mathrm{T}\ \left(\alpha_{\mathrm{p}}\right)^2/\sigma$$

$$\text{Hence, for an aqueous solution, } \delta(\mathrm{aq}) = T\ \left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^2/\sigma(\mathrm{aq})$$

$$\text{For water } (\ell) \text{ at the same T and p, } \delta_1^*(\ell) = \mathrm{T}\ \left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2/\sigma_1^*(\ell)$$

We formulate an equation for the difference, $\delta(\mathrm{aq}) - \delta_1^*(\ell)$

$$\delta(\mathrm{aq}) - \delta_1^*(\ell) = \mathrm{T}\ \left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^2/\sigma(\mathrm{aq}) - \mathrm{T}\ \left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2/\sigma_1^*(\ell)$$

We add and subtract the same term. With some slight reorganisation,

$$\begin{aligned}\delta(\mathrm{aq}) - \delta_1^*(\ell) =& \mathrm{T}\ \left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^2/\sigma(\mathrm{aq}) - \mathrm{T}\ \left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2/\sigma(\mathrm{aq}) \\ &- \mathrm{T}\ \left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2/\sigma_1^*(\ell) + \mathrm{T}\ \left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2/\sigma(\mathrm{aq})\end{aligned}$$

Or,

$$\begin{aligned}\delta(\mathrm{aq}) - \delta_1^*(\ell) =& \mathrm{T}\left[\sigma(\mathrm{aq})\right]^{-1}\left\{\left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^2 - \left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2\right\} \\ &- \mathrm{T}\ \left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2\left[\frac{1}{\sigma_1^*(\ell)} - \frac{1}{\sigma(\mathrm{aq})}\right]\end{aligned}$$

We identify the term $\left\{\left[\alpha_p(aq)\right]^2 - \left[\alpha_{p1}^*(\ell)\right]^2\right\}$ as 'a square minus a square'.

$$\begin{aligned}\delta(\mathrm{aq}) - \delta_1^*(\ell) =& \mathrm{T}\left[\sigma(\mathrm{aq})\right]^{-1}\left\{\alpha_{\mathrm{p}}(\mathrm{aq}) + \alpha_{\mathrm{p1}}^*(\ell)\right\}\left\{\alpha_{\mathrm{p}}(\mathrm{aq}) - \alpha_{\mathrm{p1}}^*(\ell)\right\} \\ &- \mathrm{T}\ \frac{\left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2}{\sigma(\mathrm{aq})\,\sigma_1^*(\ell)}\left[\sigma(\mathrm{aq}) - \sigma_1^*(\ell)\right]\end{aligned}$$

We use equations (b) for $\delta(\mathrm{aq})$ and (c) for $\delta_1^*(\ell)$ to remove explicit reference to temperature in equation (g).

$$\begin{aligned}&\delta(\mathrm{aq}) - \delta_1^*(\ell) = \\ &\delta(\mathrm{aq})\ \left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^{-2}\left\{\alpha_{\mathrm{p}}(\mathrm{aq}) + \alpha_{\mathrm{p1}}^*(\ell)\right\}\left\{\alpha_{\mathrm{p}}(\mathrm{aq}) - \alpha_{\mathrm{pl}}^*(\ell)\right\} \\ &- \delta_1^*(\ell)\left[\sigma(\mathrm{aq})\right]^{-1}\left[\sigma(\mathrm{aq}) - \sigma_1^*(\ell)\right]\end{aligned}$$

$$\text{But } \phi\left(\mathrm{K_{T_j}}\right) - \phi\left(\mathrm{K_{Sj}};\mathrm{def}\right) = \left(\mathrm{c_j}\right)^{-1}\left[\delta(\mathrm{aq}) - \delta_1^*(\ell)\right] + \delta_1^*(\ell)\,\phi\left(\mathrm{V_j}\right)$$

We insert equation (h) for the difference $\delta(\mathrm{aq}) - \delta_1^*(\ell)$ into equation (i).

$$\begin{aligned}&\phi\left(\mathrm{K_{T_j}}\right) - \phi\left(\mathrm{K_{Sj}};\mathrm{def}\right) = \\ &\frac{\delta(\mathrm{aq})\ \left[\alpha_{\mathrm{p}}(\mathrm{aq}) + \alpha_{\mathrm{p1}}^*(\ell)\right]}{\left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^2}\ \frac{\left[\alpha_{\mathrm{p}}(\mathrm{aq}) - \alpha_{\mathrm{p1}}^*(\ell)\right]}{\mathrm{c_j}} \\ &- \frac{\delta_1^*(\ell)}{\sigma(\mathrm{aq})}\ \frac{\left[\sigma(\mathrm{aq}) - \sigma_1^*(\ell)\right]}{\mathrm{c_j}} + \phi\left(\mathrm{V_j}\right)\ \delta_1^*(\ell)\end{aligned}$$

$$\text{But, } \phi\left(E_{pj}\right) = \left[c_j\right]^{-1}\ \left[\alpha_p(aq) - \alpha_{pl}^*(\ell)\right] + \alpha_{p1}^*(\ell)\,\phi\left(V_j\right)$$

We identify the difference $\left[\alpha_p(aq) - \alpha_{p1}^*(\ell)\right]$.

$$\text{Then } \phi\left(E_{pj}\right) - \alpha_{p1}^*(\ell)\,\phi\left(V_j\right) = \left[c_j\right]^{-1}\ \left[\alpha_p(aq) - \alpha_{p1}^*(\ell)\right]$$

$$\text{Similarly } \phi\left(\mathrm{C_{pj}}\right) - \sigma_1^*(\ell)\,\phi\left(\mathrm{V_j}\right) = \left[\mathrm{c_j}\right]^{-1}\left[\sigma(\mathrm{aq}) - \sigma_1^*(\ell)\right]$$

Then from equations (k), (l), (m) and (n),

$$\phi\left(\mathrm{K_{T_j}}\right)-\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)=\frac{\delta(\mathrm{aq})\ \left[\alpha_{\mathrm{p}}(\mathrm{aq})+\alpha^{*}_{\mathrm{p1}}(\ell)\right]}{\left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^{2}}\ \left[\phi\left(\mathrm{E_{pj}}\right)-\alpha^{*}_{\mathrm{p1}}(\ell)\,\phi\left(\mathrm{V_j}\right)\right]$$
$$-\frac{\delta^{*}_{1}(\ell)}{\sigma(\mathrm{aq})}\ \left[\phi\left(\mathrm{C_{pj}}\right)-\sigma^{*}_{1}(\ell)\,\phi\left(\mathrm{V_j}\right)\right]+\phi\left(\mathrm{V_j}\right)\ \delta^{*}_{1}(\ell)$$

We collect the $\phi\left(\mathrm{V_j}\right)$ terms.

$$\phi\left(\mathrm{K_{T_j}}\right)-\phi\left(\mathrm{K_{sj}};\mathrm{def}\right)=$$
$$\frac{\delta(\mathrm{aq})}{\alpha_{\mathrm{p}}(\mathrm{aq})}\left\{1+\frac{\alpha^{*}_{\mathrm{p1}}(\ell)}{\alpha_{\mathrm{p}}(\mathrm{aq})}\right\}\phi\left(\mathrm{E_{pj}}\right)-\frac{\delta^{*}_{1}(\ell)}{\sigma(\mathrm{aq})}\,\phi\left(\mathrm{C_{pj}}\right)$$
$$+\left\{-\frac{\delta(\mathrm{aq})\,\alpha^{*}_{\mathrm{p1}}(\ell)}{\alpha_{\mathrm{p}}(\mathrm{aq})}-\frac{\delta(\mathrm{aq})\ \left[\alpha^{*}_{\mathrm{p1}}(\ell)\right]^{2}}{\left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^{2}}+\frac{\delta^{*}_{1}(\ell)\,\sigma^{*}_{1}(\ell)}{\sigma(\mathrm{aq})}+\delta^{*}_{1}(\ell)\right\}\phi\left(\mathrm{V_j}\right)$$

We note that in the second {----} bracket, the product term of $\phi\left(\mathrm{V_j}\right)$. By using equations (b) for $\delta(\mathrm{aq})$ and (c) for $\delta^{*}_{1}(\ell)$ the second and third terms are together equal to zero.

Hence

$$\phi\left(\mathrm{K_{Tj}}\right)-\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)=$$
$$\frac{\delta(\mathrm{aq})}{\alpha_{\mathrm{p}}(\mathrm{aq})}\left\{1+\frac{\alpha^{*}_{\mathrm{p1}}(\ell)}{\alpha_{\mathrm{p}}(\mathrm{aq})}\right\}\phi\left(\mathrm{E_{pj}}\right)-\frac{\delta^{*}_{1}(\ell)}{\sigma(\mathrm{aq})}\,\phi\left(\mathrm{C_{pj}}\right)$$
$$+\left\{\delta^{*}_{1}(\ell)-\frac{\delta(\mathrm{aq})\,\alpha^{*}_{\mathrm{p1}}(\ell)}{\alpha_{\mathrm{p}}(\mathrm{aq})}\right\}\phi\left(\mathrm{V_j}\right)$$

The latter is the full Desnoyers–Philip equation [1]. But

$$\mathrm{limit}\,(c_j\to 0)\,\alpha_p(aq)=\alpha^{*}_{pl}(\ell)$$
$$\phi\left(E_{pj}\right)=\phi\left(E_{pj}\right)^{\infty},$$
$$\phi\left(C_{pj}\right)=\phi\left(C_{pj}\right)^{\infty},\delta(aq)=\delta^{*}_{1}(\ell)$$
$$\text{and }\sigma(aq)=\sigma^{*}_{1}(\ell)$$

$$\text{Then }\phi\left(\mathrm{K_{T_j}}\right)^{\infty}-\phi\left(\mathrm{K_{Sj};\ def\ }\right)^{\infty}=\delta^{*}_{1}(\ell)\left\{\frac{2\,\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\alpha^{*}_{\mathrm{p1}}(\ell)}-\frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\sigma^{*}_{1}(\ell)}\right\}$$

Footnotes

[1] J. E. Desnoyers and P. R. Philip, Can. J. Chem, 1972, **50**,1094.

[2] M. J. Blandamer, M. I. Davis, G. Douheret and J. C. R. Reis, Chem. Soc. Rev., 2001, **30**, 8.

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1.7.11: Compression- Isentropic- Apparent Molar Volume

A given liquid system is prepared using $\mathrm{n_1}$ moles of water, molar mass $\mathrm{M_1}$, and $\mathrm{n_j}$ moles of substance j. The closed system is at equilibrium, at temperature T and pressure p. The volume of the system is given by equation (a).

$$\mathrm{V(aq)} = \mathrm{n_1}\,\mathrm{V_1^*}(\ell) + \mathrm{n_j}\,\phi\,(\mathrm{V_j}) \tag{a}$$

Here $V_1^*(\ell)$ is the molar volume of pure water and $\phi\,(\mathrm{V_j})$ is the apparent molar volume of substance j in the system; $\mathrm{V(aq)}$ and $\phi\,(\mathrm{V_j})$ depend on the composition of the system, but $\mathrm{V_1^*}(\ell)$ does not.

The solution is perturbed to a local equilibrium state by a change in pressure along a path for which the entropy remains constant at $\mathrm{S(aq)}$. At a specified molality \(\mathrm{m}_{j the change in volume is characterised by the isentropic compressibility, $\mathrm{K_s(aq)}$ defined in equation (b).

$$\kappa_\mathrm{s}(\mathrm{aq}) = -\frac{1}{\mathrm{V(aq)}}\left(\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{p}}\right)_{\mathrm{s(aq);m(j)}} \tag{b}$$

Hence,

$$\mathrm{V(aq)}\,\mathrm{K_s(aq)} = -\mathrm{n_1}\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(aq);m(j)}} - \mathrm{n_j}\left(\frac{\partial \phi\,(\mathrm{V_j})}{\partial \mathrm{p}}\right)_{\mathrm{S(aq);m(j)}}$$

The isentropic condition on the first partial differential in equation (c) refers to the entropy of an aqueous solution at molality, m_j. There is interest in relating this partial differential to the isentropic compressibility of the pure liquid substance 1 at the same T and p, which is defined in equation (d).

$$\kappa_{\mathrm{s1}}^*(\ell) = -\frac{1}{\mathrm{V_1^*}(\ell)}\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{s^*}(\ell)} \tag{d}$$

For substance 1 the different isentropic conditions are related by equation (e).

$$\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{s^*(aq)m(j)}} = \left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{s^*}(\ell)} + \left(\frac{\partial \mathrm{S_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(aq)/m(j)}} \left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{S_1^*(l)}}\right)_{\mathrm{p^*}} \tag{e}$$

In the latter equation we identify $\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{s^*}(\ell)}$ and $\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{S_1^*(1)}}\right)_{\mathrm{p^*}}$ with, respectively, $-\mathrm{V_1^*}(\ell)\ \kappa_{\mathrm{S1}}^*(\ell)$ and $\mathrm{T}\ \alpha_{\mathrm{p1}}^*(\ell)/\sigma_1^*(\ell)$, which are thermodynamic properties of water (ℓ). Here $\sigma_1^*(\ell)$ is the heat capacitance (or heat capacity per unit volume) of water (ℓ) Using the same calculus operation, the remaining partial differential is related to an isothermal property in equation (f).

$$\left(\frac{\partial \mathrm{S_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{s^*(aq);m(j)}} = \left(\frac{\partial \mathrm{S_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{T}} + \left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{S(aq);m(j)}} \left(\frac{\partial \mathrm{S_1^*}(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{p^*}} \tag{f}$$

Since $\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{T}} = -\mathrm{V_1^*}(\ell)\ \alpha_{\mathrm{pl}}^*(\ell)$, $\left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{S(aq))m(j)}} = \mathrm{T}\ \frac{\alpha_\mathrm{p}(\mathrm{aq})}{\sigma(\mathrm{aq})}$, and $\left(\frac{\partial \mathrm{S_1^*}(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{p^*}} = \frac{\mathrm{V_1^*}(\ell)\,\sigma_1^*(\ell)}{\mathrm{T}}$, we combine these results with equation (f) to express equation (e) as equation (g).

$$\frac{1}{\mathrm{V_1^*}(\ell)}\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(aq);m(j)}} = -\kappa_{\mathrm{S1}}^*(\ell) - \mathrm{T}\,\frac{\left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2}{\sigma_1^*(\ell)} + \mathrm{T}\,\frac{\alpha_{\mathrm{p1}}^*(\ell)\,\alpha_\mathrm{p}(\mathrm{aq})}{\sigma(\mathrm{aq})} \tag{g}$$

We return to equation (c). Using equation (a) for $\mathrm{V(aq)}$, equation (c) yields equation (h).

$$-\left(\frac{\partial \phi\,(\mathrm{V_j})}{\partial \mathrm{p}}\right)_{\mathrm{s(aq);m(j)}} = \left[\left(\frac{\mathrm{n_1}}{\mathrm{n_j}}\right)\mathrm{V_1^*}(\ell) + \phi\,(\mathrm{V_j})\right]\mathrm{K_s(aq)} + \left(\frac{\mathrm{n_1}}{\mathrm{n_j}}\right)\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{s(aq);m(j)}} \tag{h}$$

We note that $\frac{\mathrm{n_1}}{\mathrm{n_j}} = \frac{1}{\mathrm{m_j\,M_1}}$ And that density $\rho_1^*(\ell) = \frac{\mathrm{M_1}}{\mathrm{V_1^*}(\ell)}$. Then combining equations (g) and (h) leads to equation (i) after slight simplification.

$$-\left(\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right)_{\mathrm{s(aq);m(j)}} =$$
$$\left[\kappa_{\mathrm{s}}(\mathrm{aq})-\kappa^{*}_{\mathrm{s1}}(\ell)\right]\left[\mathrm{m_j}\,\rho^{*}_{1}(\ell)\right]^{-1}+\kappa_{\mathrm{s}}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$
$$+\left[\mathrm{m_j}\,\rho^{*}_{1}(\ell)\right]^{-1}\,\mathrm{T}\,\alpha^{*}_{\mathrm{p1}}(\ell)\left[\frac{\alpha_{\mathrm{p}}(\mathrm{aq})}{\sigma(\mathrm{aq})}-\frac{\alpha^{*}_{\mathrm{p1}}(\ell)}{\sigma^{*}_{1}(\ell)}\right]$$

An equivalent derivation of equation (i) has been given [1].

Footnotes

[1] M. J. Blandamer, J. Chem. Soc., Faraday Trans., 1998, 94, 1057.

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1.7.12: Compressions- Isentropic- Binary Liquid Mixtures

A given liquid mixture is prepared using $\mathrm{n_1}$ moles of water and n_j moles of liquid substance j. The closed system is at equilibrium, at temperature T and pressure p. The volume of the system is defined by the following equation.

$$\mathrm{V = V\,[T, p, n_1, n_j]}$$

Similarly the entropy of the system is defined by equation (b).

$$\mathrm{S = S\,[T, p, n_1, n_j]}$$

The volume of the system is given by equation (c).

$$\mathrm{V = n_1\,V_1 + n_j\,V_j}$$

Here $\mathrm{V_1}$ and V_j are the partial molar volumes of the two substances in the system; V, $\mathrm{V_1}$ and V_j depend on the composition of the system. Similarly the entropy of the system is given by equation (d).

$$\mathrm{S = n_1\,S_1 + n_j\,S_j}$$

The molar volume of the system $\mathrm{V_m}$ is given by the ratio $\mathrm{V/\,(n_1 + n_j)}$.

$$\text{Hence,} \quad \mathrm{V_m = x_1\,V_1 + x_j\,V_j}$$

$$\text{Similarly} \quad S_m = x_1\,S_1 + x_j\,S_j$$

The system under examination is a binary liquid mixture such that the thermodynamic properties of the mixture are ideal.

$$\mathrm{V_m(mix;id) = x_1\,V_1^*(\ell) + x_j\,V_j^*(\ell)}$$

$$\mathrm{S_m(mix;id) = x_1\,S_1^*(\ell) + x_j\,S_j^*(\ell) + \Delta_{mix}S_m(mix;id)}$$

In other words the two reference states are the pure substances at the initially fixed T and p. In equation (h) the term $\mathrm{\Delta_{mix}S_m(mix;id)}$ describes the ideal molar entropy of mixing, which is a function of composition only. The liquid mixture is perturbed to a local equilibrium state by a change in pressure along a path for which the entropy remains at that given by equation (h). At a specified mole fraction x_j the change in volume is characterised by the isentropic compression, $\mathrm{K_{Sm}(mix;id)}$ which is $\mathrm{K_m}$ (at constant $\mathrm{S_m(mix;id)}$) defined in equation (i).

$$\mathrm{K_{Sm}\,(mix;x_j;id) = -\left(\frac{\partial V_m(mix;id)}{\partial p}\right)_{S(m;mix;id),x(j)}}$$

Hence,

$$\mathrm{K_{Sm}\,(mix;x_j;id) = -x_1\left(\frac{\partial V_1^*(\ell)}{\partial p}\right)_{S(m;mix;dd),x(j)} - x_j\left(\frac{\partial V_2^*(\ell)}{\partial p}\right)_{S(m;mix;id),x(j)}}$$

We note that the isentropic condition on the partial differentials in equation (j) refers to the entropy of an ideal mixture at mole fraction x_j. There is merit in relating these partial differentials to the isentropic compressions of the pure liquid substances 1 and j at the same T and p, which are defined in equations (k) and (l).

$$\mathrm{K_{si}^*(\ell) = -\left(\frac{\partial V_1^*(\ell)}{\partial p}\right)_{s(1)^*}}$$

$$\mathrm{K_{Sj}^*(\ell) = -\left(\frac{\partial V_j^*(\ell)}{\partial p}\right)_{s(j)^*}}$$

The required relationship is obtained using a calculus operation. For substance 1 the different isentropic conditions are related by equation (m).

$$\left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(m;mix;jd)\times(j)}} =$$
$$\left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(1)^*}} + \left(\frac{\partial \mathrm{S}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(m;mix;;d)\times(j)}} \left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{S}_1^*(\ell)}\right)_{\mathrm{p}}\Bigg)^*$$

In the latter equation we identify $\left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{s(1)^*}}$ and $\left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{S}_1^*(\ell)}\right)_{\mathrm{p}}$ with, respectively, $-\mathrm{K}_{\mathrm{Sl}}^*(\ell)$ and $\mathrm{T}\,\frac{\mathrm{E}_{\mathrm{pl}}^*(\ell)}{\mathrm{C}_{\mathrm{pl}}^*(\ell)}$ which are thermodynamic properties of water(ℓ). Using the same calculus operation, the remaining partial differential is related to an isothermal property in equation (n).

$$\left(\frac{\partial \mathrm{S}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(m;mix;id\ )\times(j)}} =$$
$$\left(\frac{\partial \mathrm{S}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{T}} + \left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{S(m;mix;id)\times(j)}} \left(\frac{\partial \mathrm{S}_1^*(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

But $\left(\frac{\partial \mathrm{S}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{T}} = -\mathrm{E}_{\mathrm{pl}}^*(\ell)$, $\left(\frac{\partial T}{\partial p}\right)_{\mathrm{S(m;mix;jd)x(j)}} = \mathrm{T}\,\frac{\mathrm{E}_{\mathrm{pm}}(\mathrm{A;mix;id})}{\mathrm{C}_{\mathrm{pm}}(\mathrm{A;mix;id})}$, and $\left(\frac{\partial \mathrm{S}_1^*(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \frac{\mathrm{C}_{\mathrm{pm}}^*(\ell)}{\mathrm{T}}$,

We combine these results with equation (n) to re-express equation (m) as equation (o).

$$\left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(m;mix;id)x(j)}} =$$
$$-\mathrm{K}_{\mathrm{s1}}^*(\ell) - \mathrm{T}\,\frac{\left[\mathrm{E}_{\mathrm{p1}}^*(\ell)\right]^2}{\mathrm{C}_{\mathrm{p1}}^*(\ell)} + \mathrm{T}\,\mathrm{E}_{\mathrm{p1}}^*(\ell)\,\frac{\mathrm{E}_{\mathrm{pm}}(\mathrm{mix;id})}{\mathrm{C}_{\mathrm{pm}}(\mathrm{mix;id})}$$

Similarly, for the substance j we obtain equation (p).

$$\left(\frac{\partial \mathrm{V}_{\mathrm{j}}^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{S(m;mix;dd)\times(j)}} =$$
$$-\mathrm{K}_{\mathrm{Sj}}^*(\ell) - \mathrm{T}\,\frac{\left[\mathrm{E}_{\mathrm{pj}}^*(\ell)\right]^2}{\mathrm{C}_{\mathrm{pj}}^*(\ell)} + \mathrm{T}\,\mathrm{E}_{\mathrm{pj}}^*(\ell)\,\frac{\mathrm{E}_{\mathrm{pm}}(\mathrm{mix;id})}{\mathrm{C}_{\mathrm{pm}}(\mathrm{mix;id})}$$

Equations (o) and (p) can be used to recast equation (j) in the form of equation (q).

$$\mathrm{K}_{\mathrm{Sm}}(\mathrm{mix;id}) = \mathrm{x}_1\,\mathrm{K}_{\mathrm{Sl1}}^*(\ell) + \mathrm{x}_{\mathrm{j}}\,\mathrm{K}_{\mathrm{Sj}}^*(\ell) +$$
$$\mathrm{T}\left\{\mathrm{x}_1\,\frac{\left[\mathrm{E}_{\mathrm{p1}}^*(\ell)\right]^2}{\mathrm{C}_{\mathrm{p1}}^*(\ell)} + \mathrm{x}_{\mathrm{j}}\,\frac{\left[\mathrm{E}_{\mathrm{pj}}^*(\ell)\right]^2}{\mathrm{C}_{\mathrm{pj}}^*(\ell)}\right.$$
$$\left. - \left[\mathrm{x}_1\,\mathrm{E}_{\mathrm{pl}}^*(\ell) + \mathrm{x}_{\mathrm{j}}\,\mathrm{E}_{\mathrm{pj}}^*(\ell)\right]\,\frac{\mathrm{E}_{\mathrm{pm}}(\mathrm{mix;id})}{\mathrm{C}_{\mathrm{pm}}(\mathrm{mix;id})}\right\}$$

$\mathrm{K}_{\mathrm{Sm}}(\mathrm{A;\ mix;\ id\ })$ is the ideal molar isentropic compression, which is commonly denoted by id $\mathrm{K}_{\mathrm{Sm}}^{\mathrm{id}}$. The sum, $\left[x_1\,E_{p1}^*(\ell) + x_j\,E_{pj}^*(\ell)\right]$ is the ideal molar isobaric thermal expansion E_{pm}^{id} for the binary liquid mixture, here denoted as $\mathrm{E}_{\mathrm{pm}}(\mathrm{mix;id})$, and analogously for the ideal molar isobaric heat capacity $\mathrm{C}_{\mathrm{pm}}^{\mathrm{id}} = \mathrm{C}_{\mathrm{pm}}(\mathrm{mix;id})$. Thus,

$$\mathrm{K}_{\mathrm{Sm}}(\mathrm{mix;id}) = \mathrm{x}_1\,\mathrm{K}_{\mathrm{s1}}^*(\ell) + \mathrm{x}_{\mathrm{j}}\,\mathrm{K}_{\mathrm{Sj}}^*(\ell) +$$
$$\mathrm{T}\left\{\mathrm{x}_1\,\frac{\left[\mathrm{E}_{\mathrm{pl}}^*(\ell)\right]^2}{\mathrm{C}_{\mathrm{pl}}^*(\ell)} + \mathrm{x}_{\mathrm{j}}\,\frac{\left[\mathrm{E}_{\mathrm{pj}}^*(\ell)\right]^2}{\mathrm{C}_{\mathrm{pj}}^*(\ell)} - \frac{\left[\mathrm{E}_{\mathrm{pm}}(\mathrm{mix;id})\right]^2}{\mathrm{C}_{\mathrm{pm}}(\mathrm{mix;id})}\right\}$$

The last term of equation (r) expresses a mixing property. In general terms,

$$\mathrm{K}_{\mathrm{Sm}}(\mathrm{mix;\ id\ }) = \mathrm{x}_1\,\mathrm{K}_{\mathrm{sl}}^*(\ell) + \mathrm{x}_{\mathrm{j}}\,\mathrm{K}_{\mathrm{Sj}}^*(\ell) + \Delta_{\mathrm{mix}}\,\mathrm{K}_{\mathrm{Sm}}(\mathrm{mix;id})$$

From equations (r) and (s) we obtain the following expression.

$$\Delta_{\mathrm{mix}}\,\mathrm{K_{Sm}(mix;id)} =$$
$$\mathrm{T}\left\{\mathrm{x_1}\,\frac{\left[\mathrm{E^*_{p1}}(\ell)\right]^2}{\mathrm{C^*_{p1}}(\ell)}+\mathrm{x_j}\,\frac{\left[\mathrm{E^*_{pj}}(\ell)\right]^2}{\mathrm{C^*_{pj}}(\ell)}-\frac{\left[\mathrm{E_{pm}(mix;id)}\right]^2}{\mathrm{C_{pm}(mix;id)}}\right\}$$
$$\Delta_{\mathrm{mix}}\,\mathrm{K_{Sm}(A;mix;id)} = \mathrm{T}\left\{\mathrm{x_1}\left[\mathrm{E^*_{p1}}(\ell)\right]^2/\mathrm{C^*_{p1}}(\ell)\right.$$
$$\left.+\mathrm{x_j}\left[\mathrm{E^*_{pj}}(\ell)\right]^2/\mathrm{C^*_{pj}}(\ell)-\left[\mathrm{E_{pm}(\ mix\ ;id)}\right]^2/\mathrm{C_{pm}(mix;id)}\right\}$$

This is an important, albeit frequently neglected term, in the calculation of isentropic compressions of thermodynamically ideal liquid mixtures. In general ideal molar mixing values are non-zero for non-Gibbsian properties, the origin of which has been discussed [1].

We recall the definition of an apparent molar property. Hence,

$$\mathrm{K_{Sm}(mix;id)} = \mathrm{x_1}\,\mathrm{K^*_{S1}}(\ell)+\mathrm{x_j}\,\phi\left(\mathrm{K_{S}}j\right)\mathrm{(mix;id)}$$

Here $\phi\left(\mathrm{K_{Sj}}\right)\mathrm{(mix;id)}$ is the apparent molar isentropic compression of chemical substance j in the ideal liquid mixture. Combination of equations (r) and (u) yields equation (v) [2].

$$\phi\left(\mathrm{K_{S_j}}\right)\mathrm{(mix;id)} =$$
$$\mathrm{K^*_{Sj}}(\ell)+\mathrm{T}\left\{\mathrm{x_1}\,\frac{\left[\mathrm{E^*_{pl1}}(\ell)\right]^2}{\mathrm{C^*_{pl}}(\ell)}+\mathrm{x_j}\,\frac{\left[\mathrm{E^*_{pj}}(\ell)\right]^2}{\mathrm{C^*_{pj}}(\ell)}-\frac{\left[\mathrm{E_{pm}(mix;id)}\right]^2}{\mathrm{C_{pm}(mix;id)}}\right\}/\mathrm{x_j}$$

The limiting values for $\phi\left(\mathrm{K_{Sj}}\right)$ at $\mathrm{x}_j = 1$ and $\mathrm{x}_j = 0$ are of particular interest. For the pure liquid substance j, equation (w) is readily obtained.

$$\mathrm{limit}\,(\mathrm{x_j}\to 1)\,\phi\left(\mathrm{K_{Sj}}\right)\mathrm{(mix;id)} = \mathrm{K^*_{Sj}}(\ell)$$

The latter is the expected property. However, the infinite dilution limit of equation (v) is not immediately obvious. In fact, both the numerator and denominator in the last term approach zero as we approach infinite dilution ($\mathrm{x}_j = 0$). What emerges is equation (x) [3], which is an example of the unusual formalism for non-Lewisian properties [4].

$$\mathrm{limit}\,(\mathrm{x_j}\to 0)\,\phi\left(\mathrm{K_{Sj}}\right)\mathrm{(mix;id)} =$$
$$\mathrm{K^*_{Sj}}(\ell)+\mathrm{T\,C^*_{pj}}(\ell)\left[\frac{\mathrm{E^*_{pj}}(\ell)}{\mathrm{C^*_{pj}}(\ell)}-\frac{\mathrm{E^*_{pl}}(\ell)}{\mathrm{C^*_{p1}}(\ell)}\right]^2$$

Thus for ideal liquid mixtures $\phi\left(\mathrm{K_{Sj}}\right)^{\infty}$ is given by a combination of properties for both pure liquid components. In other words, the chemical nature of component 1 affects the non-Lewisian properties of its mate j in the ideal mixture. This is in contrast with apparent molar Lewisian properties, such as $\phi\left(\mathrm{V_j}\right)$, for which the values in ideal mixtures are the same as in the pure liquid state of substance j.

An extensive literature describes isentropic compressions of binary liquid mixtures [5]

Footnotes

[1] G. Douhéret, M. I. Davis, J. C. R. Reis and M. J. Blandamer, ChemPhysChem, 2001, **2**, 148.

[2] M. I. Davis, G. Douhéret, J. C. R. Reis and M. J. Blandamer, Phys. Chem. Chem. Phys., 2001, **3**, 4555.

[3] It is instructive to show how the limiting value for $\phi\left(\mathrm{K_{Sj}}\right)\mathrm{(mix;id)}$ at $\mathrm{x}_j = 0$ (and hence $\mathrm{x}_1 = 1$) is obtained from equation (v). In this limit the last term (without T) of equation (v) becomes,

$$\mathrm{limit}\,(\mathrm{x_j}\to 0)\left\{\mathrm{x_1}\,\frac{\left[\mathrm{E^*_{p1}}(\ell)\right]^2}{\mathrm{C^*_{p1}}(\ell)}+\mathrm{x_j}\,\frac{\left[\mathrm{E^*_{pj}}(\ell)\right]^2}{\mathrm{C^*_{pj}}(\ell)}-\frac{\left[\mathrm{E_{pm}(mix;id)}\right]^2}{\mathrm{C_{pm}(mix;id)}}\right\}/0$$
$$= 0/0$$

We apply L'Hospital's rule which asserts that this limit is equal to the ratio of limits (bb) and (cc).

$$\text{limit}\,(x_j \to 0)$$
$$d\left\{ x_1 \frac{\left[E^*_{p1}(\ell)\right]^2}{C^*_{p1}(\ell)} + x_j \frac{\left[E^*_{pj}(\ell)\right]^2}{C^*_{pj}(\ell)} - \frac{\left[x_1 E^*_{p1}(\ell) + x_j E^*_{pj}(\ell)\right]^2}{x_1 C^*_{p1}(\ell) + x_j C^*_{pj}(\ell)} \right\} / dx x_j$$

$$\text{limit}\,(x_j \to 0)\, dx_j / dx_j$$

The latter limit is unity. The former is obtained from the following differential.

$$d\left\{ x_1 \frac{\left[E^*_{p1}(\ell)\right]^2}{C^*_{p1}(\ell)} + x_j \frac{\left[E^*_{pj}(\ell)\right]^2}{C^*_{pj}(\ell)} - \frac{\left[x_1 E^*_{p1}(\ell) + x_j E^*_{pj}(\ell)\right]^2}{x_1 C^*_{p1}(\ell) + x_j C^*_{pj}(\ell)} \right\} / dx x_j$$
$$= -\frac{\left[E^*_{p1}(\ell)\right]^2}{C^*_{p1}(\ell)} + \frac{\left[E^*_{pj}(\ell)\right]^2}{C^*_{pj}(\ell)}$$
$$- \left\{ 2 \frac{\left[x_1 E^*_{p1}(\ell) + x_j E^*_{pj}(\ell)\right]}{\left[x_1 C^*_{p1}(\ell) + x_j C^*_{pj}(\ell)\right]} \right\} \left[-E^*_{p1}(\ell) + E^*_{pj}(\ell)\right]$$
$$+ \left\{ \frac{\left[x_1 E^*_{p1}(\ell) + x_j E^*_{pj}(\ell)\right]^2}{\left[x_1 C^*_{p1}(\ell) + x_j C^*_{pj}(\ell)\right]^2} \right\} \left[-C^*_{p1}(\ell) + C^*_{pj}(\ell)\right]$$

The limiting value of this differential is,

$$\text{limit}\,(x_1 \to 0) \frac{d\{\ldots\}}{dx_j} = C^*_{pj}(\ell) \left[\frac{E^*_{pj}(\ell)}{C^*_{pj}(\ell)} - \frac{E^*_{p1}(\ell)}{C^*_{p1}(\ell)} \right]^2$$

This is the value for the limit of equation (aa), which was used to obtain equation (x) above.

[4] J. C. R. Reis, M. J. Blandamer, M. I. Davis and G. Douhéret, Phys. Chem. Chem. Phys., 2001, **3**, 1465.

[5]

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1.7.13: Compressions- Isothermal- Equilibrium and Frozen

The volume of a given closed system is defined by the set of independent variables T, p and composition ξ; $\mathrm{V} = \mathrm{V}[\mathrm{T}, \mathrm{p}, \xi]$. We assert that in this state the affinity for spontaneous chemical reaction is A. The system is perturbed by a change in pressure such that the system can track one of two pathways; (i) at constant A or (ii) at constant ξ. The differential dependences of volume on pressure are related using equation (a).

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} - \left(\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}} \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}}$$

The two differentials expressing the dependence of volume on pressure define the equilibrium isothermal compression and the frozen isothermal compression respectively [1]. For a system at equilibrium, (i.e. minimum in G at fixed T and p) following perturbation by a change in pressure,

$$\mathrm{K_T}(\mathrm{A}=0) = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0} \qquad \mathrm{K_T}\left(\xi^{\mathrm{eq}}\right) = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi^{\mathrm{a}}}$$

The negative signs recognise that for all thermodynamically stable systems, the volume **decreases** with **increase** in pressure. Nevertheless there is merit in thinking of compression (and compressibility) as a positive feature of a system. Both $\mathrm{K_T}\left(\xi^{\mathrm{eq}}\right)$ and $\mathrm{K_T}(\mathrm{A}=0)$ are extensive variables characterising two possible pathways. From equation (a) [2],

$$\mathrm{K_T}(\mathrm{A}=0) = \mathrm{K_T}\left(\xi^{\mathrm{eq}}\right) - \left[\left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}}\right]^2 \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}}$$

But at equilibrium, $(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}} < 0$. Hence, irrespective of the sign of $(\partial \mathrm{V}/\partial \xi)_{\mathrm{T,p}}$, $\mathrm{K_T}(\mathrm{A}=0) > \mathrm{K_T}\left(\xi^{\mathrm{eq}}\right)$. Equation (c) is rewritten in terms of compressibilities [3].

$$\kappa_{\mathrm{T}}(\mathrm{A}=0) = -(1/\mathrm{V})\,(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T,A}=0} \qquad \kappa_{\mathrm{T}}\left(\xi^{\mathrm{eq}}\right) = -(1/\mathrm{V})\,(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T},\xi^{\mathrm{eq}}}$$

$$\kappa_{\mathrm{T}}(\mathrm{A}=0) = \kappa_{\mathrm{T}}\left(\xi^{\mathrm{eq}}\right) - (1/\mathrm{V})\,\left[(\partial \mathrm{V}/\partial \xi)_{\mathrm{T,p}}\right]^2\,(\partial \xi/\partial \mathrm{A})_{\mathrm{T,p}}$$

Because $(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}} < 0$, for all stable systems, $\kappa_{\mathrm{T}}(\mathrm{A}=0) > \kappa_{\mathrm{T}}\left(\xi^{\mathrm{eq}}\right)$. According therefore to equation (e) the volume decrease accompanying a given change in pressure is more dramatic under condition that $\mathrm{A}=0$ than under the condition where ξ remains constant at ξ^{eq} [4]. Both $\kappa_{\mathrm{T}}(\mathrm{A}=0)$ and $\kappa_{\mathrm{T}}\left(\xi^{\mathrm{eq}}\right)$ are volume intensive properties of a solution [5].

Footnotes

[1] The contrast between the two conditions is familiar to anyone who has dived into a swimming pool and “got it wrong”. Hitting the wall of water is similar to the conditions for$\mathrm{K_T}(\xi)$ whereas for a good dive the conditions resemble $\mathrm{K_T}(\mathrm{A}=0)$; the water molecules move apart to allow a smooth entry into the water.

[2] Consider $\left(\frac{\partial^2 \mathrm{G}}{\partial \mathrm{p}\,\partial \xi}\right) = \left(\frac{\partial^2 \mathrm{G}}{\partial \xi\,\partial \mathrm{p}}\right)$. Then, $-\left(\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} = \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}}$

[3] $\mathrm{K_T} = \left[\mathrm{m}^3\ \mathrm{Pa}^{-1}\right]; \kappa_{\mathrm{T}} = \left[\mathrm{Pa}^{-1}\right]$

[4] Equation (e) forms the basis of the pressure-jump fast reaction technique. A rapid change in pressure produces a “frozen” system which relaxes to the equilibrium state at a rate characteristic of the system.

[5] For information concerning $\mathrm{D_2O}(\ell)$, see R. A. Fine and F. J. Millero, J.Chem.Phys.,1975,**63**,89.

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1.7.14: Compressions- Ratio- Isentropic and Isothermal

Using a calculus operation, we obtain equations relating isothermal and isentropic dependencies of volume on pressure.

Thus,

$$\begin{aligned}(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T}} &= -(\partial \mathrm{T}/\partial \mathrm{p})_{\mathrm{V}}\,(\partial \mathrm{V}/\partial \mathrm{T})_{\mathrm{p}} \\ &= -(\partial \mathrm{T}/\partial \mathrm{p})_{\mathrm{V}}\,(\partial \mathrm{V}/\partial \mathrm{S})_{\mathrm{p}}\,(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{p}}\end{aligned}$$

and,

$$\begin{aligned}(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{s}} &= -\,(\partial \mathrm{S}/\partial \mathrm{p})_{\mathrm{v}}\,(\partial \mathrm{V}/\partial \mathrm{S})_{\mathrm{p}} \\ &= -(\partial \mathrm{T}/\partial \mathrm{p})_{\mathrm{V}}\,(\partial \mathrm{V}/\partial \mathrm{S})_{\mathrm{p}}\,(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{V}}\end{aligned}$$

Then,

$$(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T}}/(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{s}} = (\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{p}}/(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{V}}$$

The Gibbs-Helmholtz equation requires that

$$\mathrm{H} = \mathrm{G} - \mathrm{T}\,(\partial \mathrm{G}/\partial \mathrm{T})_{\mathrm{p}}$$

Also

$$(\partial \mathrm{H}/\partial \mathrm{T})_{\mathrm{p}} = \mathrm{C}_{\mathrm{p}} = -\mathrm{T}\,\left(\partial^2 \mathrm{G}/\partial \mathrm{T}^2\right)_{\mathrm{p}} = \mathrm{T}\,(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{p}}$$

Similarly,

$$(\partial \mathrm{U}/\partial \mathrm{T})_{\mathrm{V}} = \mathrm{C}_{\mathrm{V}} = \mathrm{T}\,(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{V}}$$

Hence,

$$\mathrm{K}_{\mathrm{T}}/\mathrm{K}_{\mathrm{s}} = \mathrm{C}_{\mathrm{p}}/\mathrm{C}_{\mathrm{V}}$$

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1.7.15: Compression- Isentropic and Isothermal- Solutions- Limiting Estimates

The density of an aqueous solutions at defined T and p and solute molality m_j yields the apparent molar volume of solute j, $\phi\left(\mathrm{V_j}\right)$. The dependence of $\phi\left(\mathrm{V_j}\right)$ on m_j can be extrapolated to yield the limiting (infinite dilution) property $\phi\left(\mathrm{V_j}\right)^{\infty}$. The isothermal dependence of densities on pressure can be expressed in terms of an analogous infinite dilution apparent molar isothermal compression, $\phi\left(\mathrm{K_{Tj}}\right)^{\infty}$. Similarly the isentropic compressibilities of solutions are characterised by $\phi\left(\mathrm{K_{S}}j;\mathrm{def}\right)^{\infty}$ which is accessible via the density of a solution and the speed of sound in the solution. Nevertheless the isothermal property $\phi\left(\mathrm{K_{T_j}}\right)^{\infty}$ presents fewer conceptual problems in terms of understanding the properties of solutes and solvents which control volumetric properties. The challenge is to use $\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^{\infty}$ in order to obtain $\phi\left(\mathrm{K_{Tj}}\right)^{\infty}$. The linking relationship is the Desnoyers-Philip equation [1]. The apparent molar isothermal compression for solute $j\phi\left(\mathrm{K_{T_j}}\right)$ is related to the concentration c_j of solute using equation (a) where $\phi\left(V_j\right)$ is the apparent molar volume of the solute.

$$\phi\left(K_{\mathrm{T_j}}\right)=\left[\kappa_{\mathrm{T}}(\mathrm{aq})-\kappa^{*}_{\mathrm{Tl}}(\ell)\right]\,\left(\mathrm{c_j}\right)^{-1}+\kappa^{*}_{\mathrm{Tl}}(\ell)\,\phi\left(\mathrm{V_j}\right)$$

The corresponding isentropic compression for solute j, $\phi\left(K_{\mathrm{Sj}};\ \mathrm{def}\ \right)$ is related to the concentration c_j using equation (b).

$$\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)\equiv\left[\kappa_{\mathrm{S}}(\mathrm{aq})-\kappa^{*}_{\mathrm{S1}}(\ell)\right]\,\left(\mathrm{c_j}\right)^{-1}+\kappa^{*}_{\mathrm{S1}}(\ell)\,\phi\left(\mathrm{V_j}\right)$$

[We replace the symbol ≡ by the symbol = in the following account.]

$$\text{By definition }\delta(\mathrm{aq})=\kappa_{\mathrm{T}}(\mathrm{aq})-\kappa_{\mathrm{S}}(\mathrm{aq})$$

$$\text{And }\delta^{*}_{1}(\ell)=\kappa^{*}_{\mathrm{T1}}(\ell)-\kappa^{*}_{\mathrm{S1}}(\ell)$$

Hence $\phi\left(\mathrm{K_{T_j}}\right)$ and $\phi\left(K_{\mathrm{Sj}};\mathrm{def}\right)$ are related by equation (e).

$$\phi\left(\mathrm{K_{T_j}}\right)-\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)=\left(\mathrm{c_j}\right)^{-1}\,\left[\delta(\mathrm{aq})-\delta^{*}_{1}(\ell)\right]+\delta^{*}_{1}(\ell)\,\phi\left(\mathrm{V_j}\right)$$

The difference $\phi\left(\mathrm{K_{T_j}}\right)-\phi\left(\mathrm{K_{S_j}};\mathrm{def}\right)$ depends on the concentration of the solute c_j. Further $\delta(\mathrm{aq})-\delta^{*}_{1}(\ell)$ is not zero. In fact,

$$\begin{aligned}\delta(\mathrm{aq})-\delta^{*}_{1}(\ell)=&\\ &\left\{\mathrm{T}\,\left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^{2}/\sigma(\mathrm{aq})-\left\{\mathrm{T}\,\left[\alpha^{*}_{\mathrm{p1}}(\ell)\right]^{2}/\sigma^{*}_{1}(\ell)\right\}\end{aligned}$$

Using the technique of adding and subtracting the same quantity, equation (f) is re-expressed as follows.

$$\begin{aligned}\delta(\mathrm{aq})-\delta^{*}_{1}(\ell)=&\\ \left\{\delta(\mathrm{aq})/\left[\alpha_{\mathrm{p}}(\mathrm{aq})\right]^{2}\right\}\,&\left[\alpha_{\mathrm{p}}(\mathrm{aq})+\alpha^{*}_{\mathrm{p1}}(\ell)\right]\,\left[\alpha_{\mathrm{p}}(\mathrm{aq})-\alpha^{*}_{\mathrm{p1}}(\ell)\right]\\ &-\left[\delta^{*}_{1}(\ell)/\sigma(\mathrm{aq})\right]\,\left[\sigma(\mathrm{aq})-\sigma^{*}_{1}(\ell)\right]\end{aligned}$$

The difference $\left[\alpha_{\mathrm{p}}(\mathrm{aq})-\alpha^{*}_{\mathrm{p1}}(\ell)\right]$ is related to $\phi\left(\mathrm{E_{pj}}\right)$ using equation (h).

$$\phi\left(E_{pj}\right)=\left[\alpha_{p}(aq)-\alpha^{*}_{p1}(\ell)\right]\,\left(c_j\right)^{-1}+\alpha^{*}_{p1}(\ell)\,\phi\left(V_j\right)$$

Similarly, $\left[\sigma(\mathrm{aq})-\sigma^{*}_{1}(\ell)\right]$ is related to $\phi\left(C_{pj}\right)$ using equation (i).

$$\phi\left(C_{pj}\right)=\left[\sigma(aq)-\sigma^{*}_{1}(\ell)\right]\,\left(c_j\right)^{-1}+\sigma^{*}_{1}(\ell)\,\phi\left(V_j\right)$$

Using equations (g) - (i), we express equation (e) as follows.

$$\begin{aligned}\phi\left(\mathrm{K_{T_j}}\right)-\phi\left(\mathrm{K_{sj}};\mathrm{def}\right)=&\\ \left[\delta(\mathrm{aq})/\alpha_{\mathrm{p}}(\mathrm{aq})\right]\,\left\{1+\left[\alpha^{*}_{\mathrm{p1}}(\ell)/\alpha_{\mathrm{p}}(\mathrm{aq})\right]\right\}\,\phi\left(\mathrm{E_{pj}}\right)&\\ -\left[\delta^{*}_{1}(\ell)/\sigma(\mathrm{aq})\right]\,\phi\left(\mathrm{C_{pj}}\right)+\left\{\delta^{*}_{1}(\ell)\right.&\\ \left.-\left[\delta(\mathrm{aq})\,\alpha^{*}_{\mathrm{p1}}(\ell)/\alpha_{\mathrm{p}}(\mathrm{aq})\right]\right\}\,\phi\left(\mathrm{V_j}\right)&\end{aligned}$$

Equation (j) was obtained by Desnoyers and Philip [1] who showed that if $\phi\left(K_{T_j}\right)^{\infty}$ and $\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^{\infty}$ are the limiting (infinite dilution) apparent molar properties, the difference is given by equation (k).

$$\begin{aligned}\phi\left(\mathrm{K_{Tj}}\right)^{\infty}-\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^{\infty}=&\\ \delta^{*}_{1}(\ell)\,\left\{\left[2\,\phi\left(\mathrm{E_{pj}}\right)^{\infty}/\alpha^{*}_{\mathrm{pl1}}(\ell)\right]-\left[\phi\left(\mathrm{C_{pj}}\right)^{\infty}/\sigma^{*}_{1}(\ell)\right]\right\}&\end{aligned}$$

Using equation (b), $\phi\left(K_{\mathrm{Sj}};\ \mathrm{def}\ \right)$ is plotted as a function of cj across a set of different solutions having different entropies. $\mathrm{Limit}\left(\mathrm{c_j} \rightarrow 0\right) \phi\left(\mathrm{K_{Sj}};\ \mathrm{def}\ \right)$ defines $\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^{\infty}$. Granted two limiting quantities, $\phi\left(E_{pj}\right)^{\infty}$ and $\phi\left(C_{pj}\right)^{\infty}$ are available for the solution at the same T and p, equation (k) is used to calculate $\phi\left(\mathrm{K_{T_j}}\right)^{\infty}$ using $\phi\left(K_{\mathrm{S_j}};\ \mathrm{def}\ \right)^{\infty}$.

An alternative form of equation (j) refers to a solution, molality mj [2].

$$\begin{aligned}&\phi\left(\mathrm{K_{Tj}}\right)-\phi\left(\mathrm{K_{Sj}};\ \mathrm{def}\ \right)= \\ &\quad \delta_1^*(\ell)\left\{\left[2\,\phi\left(\mathrm{E_{pj}}\right)/\alpha_{\mathrm{p1}}^*(\ell)\right]-\left[\phi\left(\mathrm{C_{pj}}\right)/\sigma_1^*(\ell)\right]\right. \\ &\quad \left.+\left[\rho_1^*(\ell)\,\mathrm{m_j}\ \left[\phi\left(\mathrm{E_{pj}}\right)\right]^2/\left[\alpha_{\mathrm{p1}}^*(\ell)\right]^2\right\}\left\{1+\left[\rho_1^*(\ell)\,\mathrm{m_j}\,\phi\left(\mathrm{C_{pj}}\right)/\sigma_1^*(\ell)\right]\right\}^{-1}\end{aligned}$$

The fact that $\phi\left(\mathrm{K_{T_j}}\right)^{\infty}$ can be obtained from $\phi\left(\mathrm{K_{Sj}};\ \mathrm{def}\ \right)^{\infty}$ indicates the importance of the Desnoyers-Philip equation. Bernal and Van Hook [3] used the Desnoyers-Philip equation to calculate $\phi\left(\mathrm{K_{T_j}}\right)^{\infty}$ for glucose(aq), sucrose(aq) and fructose(aq) at $348\ \mathrm{K}$. Similarly Hedwig et. al. used the Desnoyers –Philip equation to obtain estimates of $\phi\left(K_{\mathrm{Tj}}\right)^{\infty}$ for glycyl dipeptides (aq) at $298\ \mathrm{K}$ [4].

Footnotes

[1] J. E. Desnoyers and P. R. Philip, Can. J.Chem.,1972, **50**,1095.

[2] J. C. R. Reis, J. Chem. Soc. Faraday Trans.,1998,**94**,2385.

[3] P. J. Bernal and W. A. Hook, J.Chem.Thermodyn.,1986,**18**,955.

[4] G. R. Hedwig, J. D. Hastie and H. Hoiland, J. Solution Chem.,1996, **25**, 615.

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1.7.16: Compressions- Isentropic and Isothermal- Apparent Molar Volume

A given solution is perturbed by a change in pressure to a neighbouring state at constant affinity, A.

$$(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{s}} = (\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T}} - (\partial \mathrm{S}/\partial \mathrm{p})_{\mathrm{T}} \, (\partial \mathrm{T}/\partial \mathrm{S})_{\mathrm{p}} \, (\partial \mathrm{V}/\partial \mathrm{T})_{\mathrm{p}}$$

But for the pure solvent (at constant affinity A) S * 1 * S1 K (l) = −(∂V (l)/ ∂p) and T * 1 * T1 K (l) = −(∂V (l)/ ∂p) (b)

We confine attention to perturbation at 'A = 0'; i.e. an equilibrium process. [Note the change in sign.]

$$\mathrm{K}^{*}_{\mathrm{s1}}(\ell) = \mathrm{K}^{*}_{\mathrm{T1}}(\ell) + (\partial \mathrm{S}^{*}_{1}(\ell)/\partial \mathrm{p})_{\mathrm{T}} \, (\partial \mathrm{T}/\partial \mathrm{S}^{*}_{1}(\ell))_{\mathrm{p}} \, (\partial \mathrm{V}^{*}_{1}(\ell)/\partial \mathrm{T})_{\mathrm{p}}$$

From a Maxwell Equation,

$$(\partial \mathrm{S}^{*}_{1}(\ell)/\partial \mathrm{p})_{\mathrm{T}} = -\,(\partial \mathrm{V}^{*}_{1}(\ell)/\partial \mathrm{T})_{\mathrm{p}}$$

From the Gibbs-Helmholtz Equation,

$$(\partial \mathrm{S}^{*}_{1}(\ell)/\partial \mathrm{T})_{\mathrm{p}} = \mathrm{C}^{*}_{\mathrm{p1}}(\ell)/\mathrm{T}$$

$C^{*}_{p1}(\ell)$ is the molar (equilibrium) isobaric heat capacity of the solvent at defined T and p. From equation (c), [Note change of sign.]

$$\mathrm{K}^{*}_{\mathrm{S1}}(\ell) = \mathrm{K}^{*}_{\mathrm{T1}}(\ell) - \left[(\partial \mathrm{V}^{*}_{1}(\ell)/\partial \mathrm{T})_{\mathrm{p}}\right]^{2} \, \mathrm{T}/\mathrm{C}^{*}_{\mathrm{p1}}(\ell)$$

But

$$\alpha^{*}_{1}(\ell) \, V^{*}_{1}(\ell) = (\partial V^{*}_{1}(\ell)/\partial T)_{p}$$

$$\mathrm{K}^{*}_{\mathrm{S1}}(\ell) = \mathrm{K}^{*}_{\mathrm{T1}}(\ell) - [\alpha^{*}_{1}(\ell) \, \mathrm{V}^{*}_{1}(\ell)]^{2} \, \mathrm{T}/\mathrm{C}^{*}_{\mathrm{p1}}(\ell)$$

But the ratio of isobaric heat capacity of the solvent to its molar volume,

$$\mathrm{C}^{*}_{\mathrm{p1}}(\ell)/\mathrm{V}^{*}_{1}(\ell) = \sigma^{*}_{1}(\ell).$$

$$\mathrm{K}^{*}_{\mathrm{s1}}(\ell) = \mathrm{K}^{*}_{\mathrm{T1}}(\ell) - \left[\alpha^{*}_{1}(\ell)\right]^{2} \, \mathrm{V}^{*}_{1}(\ell)\Big] \, \mathrm{T}/\sigma^{*}_{1}(\ell)$$

But

$$\kappa^{*}_{\mathrm{s1}}(\ell) = [\mathrm{V}^{*}_{1}(\ell)]^{-1} \, \mathrm{K}^{*}_{\mathrm{S1}}(\ell) \text{ and } \kappa^{*}_{\mathrm{T1}}(\mathrm{l}) = [\mathrm{V}^{*}_{1}(\ell)]^{-1} \, \mathrm{K}^{*}_{\mathrm{T1}}(\ell)$$

$$\kappa^{*}_{\mathrm{S1}}(\ell) = \kappa^{*}_{\mathrm{T1}}(\ell) - [\alpha^{*}_{1}(\ell)]^{2} \, \mathrm{T}/\sigma^{*}_{1}(\ell)$$

Similarly for an aqueous solution, molality m_{j},

$$\kappa_{\mathrm{S}}(\mathrm{aq}) = \kappa_{\mathrm{T}}(\mathrm{aq}) - [\alpha(\mathrm{aq})]^{2} \, \mathrm{T}/\sigma(\mathrm{aq})$$

Also

$$\mathrm{K}_{\mathrm{T}}(\mathrm{aq}) = \mathrm{n}_{1} \, \mathrm{K}^{*}_{\mathrm{T1}}(\ell) + \mathrm{n}_{\mathrm{j}} \, \phi\left(\mathrm{K}_{\mathrm{T_j}}\right)$$

$$\phi\left(\mathrm{K}_{\mathrm{T_j}}\right) = (\mathrm{n}_{\mathrm{j}})^{-1} \, \{\mathrm{K}_{\mathrm{T}}(\mathrm{aq}) - \mathrm{n}_{1} \, \mathrm{K}^{*}_{\mathrm{T1}}(\ell)]$$

We convert from compressions to compressibilities.

$$\phi\left(\mathrm{K}_{\mathrm{T_j}}\right) = (\mathrm{n}_{\mathrm{j}})^{-1} \, \{\mathrm{V}(\mathrm{aq}) \, \kappa_{\mathrm{T}}(\mathrm{aq}) - \mathrm{n}_{1} \, \mathrm{V}^{*}_{\mathrm{T1}}(\ell) \, \kappa^{*}_{\mathrm{T1}}(\ell)]$$

But we know $\kappa_{\mathrm{T}}(\mathrm{aq})$ in terms of) $\kappa_{\mathrm{S}}(\mathrm{aq})$ (aq [see equation (m)] and $\kappa^{*}_{\mathrm{T1}}(\ell)$ in terms of $\kappa^{*}_{\mathrm{s1}}(\ell)$. Then [NB change of sign]

$$\phi\left(\mathrm{K}_{\mathrm{T_j}}\right) = \left[\frac{\mathrm{V}(\mathrm{aq})}{\mathrm{n}_{\mathrm{j}}}\right] \left[\mathrm{K}_{\mathrm{S}}(\mathrm{aq}) + \frac{\{\alpha(\mathrm{aq})\}^{2} \, \mathrm{T}}{\sigma(\mathrm{aq})}\right] - \left[\frac{\mathrm{n}_{1} \, \mathrm{V}^{*}_{1}(\ell)}{\mathrm{n}_{\mathrm{j}}}\right] \left[\kappa^{*}_{\mathrm{Sl}}(\ell) + \frac{\{\alpha^{*}_{1}(\ell)\}^{2} \, \mathrm{T}}{\sigma^{*}_{1}(\ell)}\right]$$

We introduce densities into equation (q). For a solution having mass w,

$$\begin{aligned} \mathrm{V(aq)/n_j} &= [1/\mathrm{n_j}]\ [\mathrm{w}/\rho(\mathrm{aq})] = [1/\mathrm{n_j}\,\rho(\mathrm{aq})]\ [\mathrm{n_j\,M_j + n_1\,M_1}] \\ &= [1/\mathrm{m_j}\,\rho(\mathrm{aq})] + [\mathrm{M_j}/\rho(\mathrm{aq})] \end{aligned}$$

Also,

$$\mathrm{n_1\,V_1^*(\ell)/n_j} = [\mathrm{n_1/n_j}]\ [\mathrm{M_1}/\rho_1^*(\ell)] = [\mathrm{m_j}\,\rho_1^*(\ell)]^{-1}$$

From equations (q), (r) and (s),

$$\begin{aligned} \phi\left(\mathrm{K_{Tj}}\right) = \left[\frac{1}{\mathrm{m_j}\,\rho(\mathrm{aq})} + \frac{\mathrm{M_j}}{\rho(\mathrm{aq})}\right]\left[\kappa_\mathrm{s}(\mathrm{aq}) + \frac{\{\alpha(\mathrm{aq})\}^2\,\mathrm{T}}{\sigma(\mathrm{aq})}\right] \\ - \left[\frac{1}{\mathrm{m_j}\,\rho_1^*(\ell)}\right]\left[\kappa_{\mathrm{s1}}^*(\ell) + \frac{\{\alpha_1^*(\ell)\}^2\,\mathrm{T}}{\sigma_1^*(\ell)}\right] \end{aligned}$$

We factor out the six terms . The order in which we write these terms anticipates the next but one step.

$$\begin{aligned} \phi\left(\mathrm{K_{T_j}}\right) = \left[\frac{\kappa_\mathrm{s}(\mathrm{aq})}{\mathrm{m_j}\,\rho(\mathrm{aq})}\right] - \left[\frac{\kappa_{\mathrm{Sl}}^*(\ell)}{\mathrm{m_j}\,\rho_1^*(\ell)}\right] + \left[\frac{\mathrm{M_j}\,\kappa_\mathrm{s}(\mathrm{aq})}{\rho(\mathrm{aq})}\right] \\ + \left[\frac{\{\alpha(\mathrm{aq})\}^2\,\mathrm{T}}{\mathrm{m_j}\,\rho(\mathrm{aq})\,\sigma(\mathrm{aq})}\right] \\ - \left[\frac{\{\alpha_1^*(\ell)\}^2\,\mathrm{T}}{\mathrm{m_j}\,\rho_1^*(\ell)\,\sigma_1^*(\ell)}\right] + \left[\frac{\mathrm{M_j}\,\{\alpha(\mathrm{aq})\}^2\,\mathrm{T}}{\rho(\mathrm{aq})\,\sigma(\mathrm{aq})}\right] \end{aligned}$$

Hence,

$$\begin{aligned} \phi\left(\mathrm{K_{T_j}}\right) = \{\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_1^*(\ell)\}^{-1}\ [\{\mathrm{K_s(aq)}\,\rho_1^*(\ell)\} - \{\kappa_{\mathrm{s1}}^*(\ell)\,\rho(\mathrm{aq})\}] \\ + \{\kappa_\mathrm{S}(\mathrm{aq})\,\mathrm{M_j}/\rho(\mathrm{aq}) + \mathrm{A} + \mathrm{B} \end{aligned}$$

where,

$$\mathrm{A} = \left[\frac{\mathrm{T}}{\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_1^*(\ell)}\right]\left[\left(\frac{\{\alpha(\mathrm{aq})\}^2\,\rho_1^*(\ell)}{\sigma(\mathrm{aq})}\right) - \left(\frac{\{\alpha_1^*(\ell)\,\rho(\mathrm{aq})}{\sigma_1^*(\ell)}\right)\right]$$

and

$$\mathrm{B} = \mathrm{M_j}\,\{\alpha(\mathrm{aq})\}^2\,\mathrm{T}/\rho(\mathrm{aq})\,\sigma(\mathrm{aq})$$

With reference to solutions we compare the isentropic and isothermal dependences of $\phi\,(V_j)$ on pressure.

$$\left[\frac{\partial\phi\,(V_\mathrm{j})}{\partial\mathrm{p}}\right]_{\mathrm{S(aq)}} = \left[\frac{\partial\phi\,(\mathrm{V_j})}{\partial\mathrm{p}}\right]_\mathrm{T} - \left[\frac{\partial\mathrm{S(aq)}}{\partial\mathrm{p}}\right]_\mathrm{T}\left[\frac{\partial\mathrm{T}}{\partial\mathrm{S(aq)}}\right]_\mathrm{p}\left[\frac{\partial\phi\,(\mathrm{V_j})}{\partial\mathrm{T}}\right]_\mathrm{p}$$

Noting signs [cf. equations (d) and (e)] and the definition of $\phi\left(\mathrm{K_{T_j}}\right)$,

$$\left[\frac{\partial\phi\,(\mathrm{V_j})}{\partial\mathrm{p}}\right]_{\mathrm{S(aq)}} = -\phi\left(\mathrm{K_{T_{j_j}}}\right) - \left[-\left[\frac{\partial\mathrm{V(aq)}}{\partial\mathrm{T}}\right]_\mathrm{p}\right]\left[\frac{\mathrm{T}}{\mathrm{C_p(aq)}}\right]\left[\frac{\partial\phi\,(\mathrm{V_j})}{\partial\mathrm{T}}\right]_\mathrm{p}$$

$$\left[\frac{\partial\phi\,(\mathrm{V_j})}{\partial\mathrm{p}}\right]_{\mathrm{S(aq)}} = \phi\left(\mathrm{K_{Tj}}\right) - \left[\frac{\partial\mathrm{V(aq)}}{\partial\mathrm{T}}\right]_\mathrm{p}\left[\frac{\mathrm{T}}{\mathrm{C_p(aq)}}\right]\left[\frac{\partial\phi\,(\mathrm{V_j})}{\partial\mathrm{T}}\right]_\mathrm{p}$$

We turn our attention to $[\partial\phi\,(\mathrm{V_j})\,/\partial\mathrm{T}]_\mathrm{p}$. We recall that

$$\mathrm{V(aq)} = \mathrm{n_1\,V_1^*(\ell) + n_j\,\phi\,(V_j)}$$

$$\phi\,(\mathrm{V_j}) = (1/\mathrm{n_j})\ \mathrm{V(aq)} - [(\mathrm{n_1/n_j})\ \mathrm{V_1^*(\ell)}]$$

Hence

$$\left[\frac{\partial\phi\,(\mathrm{V_j})}{\partial\mathrm{T}}\right]_\mathrm{p} = \frac{1}{\mathrm{n_j}}\left[\frac{\partial\mathrm{V(aq)}}{\partial\mathrm{T}}\right]_\mathrm{p} - \frac{\mathrm{n_1}}{\mathrm{n_j}}\left[\frac{\partial\mathrm{V_1^*(\ell)}}{\partial\mathrm{T}}\right]_\mathrm{p}$$

We combine equations (za) and (zd). Hence

$$-\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right]_{\mathrm{S(aq)}}=$$
$$\phi\left(\mathrm{K}_{\mathrm{T_j}}\right)$$
$$-\left[\left[\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right]_{\mathrm{p}}\right]_{\mathrm{T}}\left[\frac{\mathrm{T}}{\mathrm{C_p(aq)}}\right]\left[\frac{1}{\mathrm{n_j}}\left[\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right]_{\mathrm{p}}-\frac{\mathrm{n_1}}{\mathrm{n_j}}\left[\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{T}}\right]_{\mathrm{p}}\right]$$

Or,

$$-\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}]_{\mathrm{S(aq)}}}\right]=\phi\left(\mathrm{K}_{\mathrm{T_j}}\right)$$
$$-\left[\frac{\mathrm{T}}{\mathrm{C_p(aq)}}\right]\frac{1}{\mathrm{n_j}}\left[\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right]_{\mathrm{p}}^{2}$$
$$+\left[\frac{\mathrm{T}}{\mathrm{C_p(aq)}}\right]\left[\frac{\mathrm{n_1}}{\mathrm{n_j}}\left[\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right]_{\mathrm{p}}\left[\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{T}}\right]_{\mathrm{p}}\right]$$

But

$$\alpha(\mathrm{aq})\,\mathrm{V(aq)}=[\partial \mathrm{V(aq)}/\partial \mathrm{T}]_{\mathrm{p}}$$

And

$$\alpha_1^*(\ell)\,V_1^*(\ell)=[\partial V_1^*(\ell)/\partial \mathrm{T}]_{\mathrm{p}}$$

We introduce the latter two equations into equation (zf).

$$\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right]_{\mathrm{S(aq)}}=\phi\left(\mathrm{K}_{\mathrm{T_j}}\right)$$
$$-\left[\frac{\mathrm{T}}{\mathrm{C_p(aq)}}\right]\frac{1}{\mathrm{n_j}}\left[\mathrm{V(aq)}\,\alpha(\mathrm{aq})\right]^2$$
$$+\left[\frac{\mathrm{T}}{\mathrm{C_p(aq)}}\right]\left[\frac{\mathrm{n_1}}{\mathrm{n_j}}\right]\left[\alpha(\mathrm{aq})\,\mathrm{V(aq)}\,\alpha_1^*(\ell)\,\mathrm{V_1^*}(\ell)\right]$$

But $\sigma(\mathrm{aq})=\mathrm{C_p(aq)/V(aq)}$ and $\sigma_1^*(\ell)=\mathrm{C_{p1}^*}(\ell)/\mathrm{V_1^*}(\ell)$. Also $\mathrm{M_1/V_1^*}(\ell)=\rho_1^*(\ell)$. Hence,

$$-\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right]_{\mathrm{S(aq)}}=\phi\left(\mathrm{K}_{\mathrm{T_j}}\right)$$
$$-\left[\frac{\mathrm{T}}{\sigma(\mathrm{aq})}\right]\frac{1}{\mathrm{n_j}}\,\mathrm{V(aq)}\left[\alpha(\mathrm{aq})\right]^2$$
$$+\left[\frac{\mathrm{T}}{\sigma(\mathrm{aq})}\right]\left[\frac{\mathrm{n_1}}{\mathrm{n_j}}\right]\left[\alpha(\mathrm{aq})\,\alpha_1^*(\ell)\,\mathrm{M_1}/\rho_1^*(\ell)\right]$$

Also, $\mathrm{n_j/n_1\,M_1}=\mathrm{m_j}$. And [2] $\mathrm{V(aq)/n_j}=[1/\mathrm{m_j}\,\rho(\mathrm{aq})]+[\mathrm{M_j}/\rho(\mathrm{aq})]$

Hence we obtain a relation between the two compressions of the apparent molar volumes

$$-\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right]_{\mathrm{S(aq)}}=\phi\left(\mathrm{K}_{\mathrm{T_j}}\right)$$
$$-\left[\frac{\mathrm{T}}{\sigma(\mathrm{aq})}\right]\left[\frac{1}{\mathrm{m_j}\,\rho(\mathrm{aq})}+\frac{\mathrm{M_j}}{\rho(\mathrm{aq})}\right]\left[\alpha(\mathrm{aq})\right]^2$$
$$+\left[\frac{\mathrm{T}}{\sigma(\mathrm{aq})}\right]\left[\frac{1}{\mathrm{m_j}\,\rho_1^*(\ell)}\right]\alpha(\mathrm{aq})\,\alpha_1^*(\ell)$$

Footnotes

[1] Unit check on equation (l). $\left[\mathrm{Nm^{-2}}\right]^{-1}=\left[\mathrm{Nm^{-2}}\right]^{-1}-\left\{\left[\mathrm{K^{-1}}\right]^2\left[\mathrm{K}\right]\right\}/\left[\mathrm{JK^{-1}\ mol^{-1}}\right]\left[\mathrm{m^3\ mol^{-1}}\right]^{-1}\Big\}$
$\left[\mathrm{Nm^{-2}}\right]^{-1}=\left[\mathrm{Nm^{-2}}\right]^{-1}-\left[\mathrm{Jm^{-3}}\right]^{-1}$ But $\left[\mathrm{Nm^{-2}}\right]=\left[\mathrm{Jm^{-3}}\right]$

[2] From

$$V(aq) = \frac{w}{\rho(aq)} = \frac{n_1 M_1}{\rho(aq)} + \frac{n_j M_j}{\rho(aq)}$$

$$\frac{V(aq)}{n_j} = \frac{n_1 M_1}{n_j \rho(aq)} + \frac{M_j}{\rho(aq)}$$

$$\frac{V(aq)}{n_j} = \frac{1}{m_j \rho(aq)} + \frac{M_j}{\rho(aq)}$$

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1.7.17: Compressions- Isothermal- Solutes- Partial Molar Compressions

A given aqueous solution at temperature T and near ambient pressure p contains a solute j at molality m_j. The chemical potential $\mu_j(\mathrm{aq})$ is related to the molality m_j using equation (a).

$$\mu_{\mathrm{j}}(\mathrm{aq}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}/\mathrm{m}^{0}\right) + \mathrm{R\,T\ ln}\left(\gamma_{\mathrm{j}}\right)$$

Then

$$\mathrm{V_j(aq)} = \mathrm{V_j^{\infty}(aq)} + \mathrm{R\,T}\ \left[\partial \ln\left(\gamma_{\mathrm{j}}\right)/\partial \mathrm{p}\right]_{\mathrm{T}}$$

By definition, the partial molar isothermal compression of solute j,[1]

$$K_{T_j}(aq) = -\left(\frac{\partial V_j(aq)}{\partial p}\right)_T$$

Then

$$\mathrm{K_{Tj}(aq)} = \mathrm{K_{TJ}^{\infty}(aq)} - \mathrm{R\,T}\ \left[\partial^2 \ln\left(\gamma_{\mathrm{j}}\right)/\partial \mathrm{p}^2\right]_{\mathrm{T}}$$

Thus by definition,

$$\mathrm{limit}\left(\mathrm{m_j} \rightarrow 0\right) \mathrm{K_{T_j}(aq)} = \mathrm{K_{T_j}^{\infty}(aq)}$$

Hence the difference between $\mathrm{K_{Tj}(aq)}$ and $\mathrm{K_{T_j}^{\infty}(aq)}$ depends on the second differential of $\ln\left(\gamma_j\right)$ with respect to pressure.

Footnotes

[1] The formal definition of $\mathrm{K_{Tj}(aq)}$ is given by equation (a).

$$\mathrm{K_{Tj}(aq)} = \left(\frac{\partial \mathrm{K_T}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}}$$

However,

$$\mathrm{K_T} = -(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T,n(j)}}$$

Then,

$$\mathrm{K_{Tj}(aq)} = -\left(\frac{\partial\left(\partial \mathrm{V}/\partial \mathrm{n_j}\right)_{\mathrm{T,p,n(i\neq j)}}}{\partial \mathrm{p}}\right)_{\mathrm{T,n(j)}}$$

Or,

$$\mathrm{K_{Tj}(aq)} = -\left(\frac{\partial \mathrm{V_j(aq)}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

In other words, equation (c) shows that $\mathrm{K_{Tj}(aq)}$ is a Lewisian partial molar property

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1.7.18: Compressions- Isothermal- Apparent Molar Compression

The volume of a given solution prepared at fixed temperature and fixed pressure using n_1 moles of water and n_j moles of solute j is given by equation (a).

$$\mathrm{V(aq)} = \mathrm{n}_1\,\mathrm{V}_1\mathrm{(aq)} + \mathrm{n_j}\,\mathrm{V_j(aq)}$$

If the solution is prepared using $1\ \mathrm{kg}$ of water(ℓ),

$$\mathrm{V\,(aq;\, w_1 = 1\ kg)} = \mathrm{M_1^{-1}}\,\mathrm{V}_1\mathrm{(aq)} + \mathrm{m_j}\,\mathrm{V_j(aq)}$$

M_1 is the molar mass of the solvent, water(ℓ); $\mathrm{V}_1\mathrm{(aq)}$ and $\mathrm{V}_j\mathrm{(aq)}$ are the partial molar volumes of water and solute j respectively in the solution. As we change m_j (for a fixed mass of solvent) so both $\mathrm{V}_1\mathrm{(aq)}$ and $\mathrm{V}_j\mathrm{(aq)}$ change. An important procedure rewrites equation (b) in the following form where $\mathrm{V}_1^*(\ell)$ is the molar volume of pure solvent at the same T and p. Thus,

$$\mathrm{V\,(aq;\, w_1 = 1\ kg)} = \mathrm{M_1^{-1}}\,\mathrm{V}_1^*(\ell) + \mathrm{m_j}\,\phi\,(\mathrm{V_j})$$

$\phi\,(\mathrm{V_j})$ is the apparent molar volume of the solute j. The system, an aqueous solution, is displaced by a change in pressure (at fixed T) along a path where the affinity for spontaneous change is zero. In other words the system is subjected to an equilibrium displacement. The isothermal differential dependence of volume $\mathrm{V\,(aq;\, w_1 = 1\ kg)}$ is given by equation (d).

$$\left(\frac{\partial \mathrm{V\,(aq;\, w_1 = 1\ kg}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \mathrm{M_1^{-1}}\left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{T}} + \mathrm{m_j}\left(\frac{\partial \phi\,(\mathrm{V_j})}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

By definition, the apparent molar (isothermal) compression of the solute, [1-3]

$$\phi\,(\mathrm{K_{Tj}}) = -\left(\frac{\partial \phi\,(\mathrm{V_j})}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

Similarly for equilibrium molar compression of the pure solvent,

$$\mathrm{K_{T1}^*}(\ell) = -\left(\frac{\partial \mathrm{V}_1^*(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

By definition,

$$\mathrm{K_T\,(aq;\, w_1 = 1\ kg)} = -\left(\frac{\partial \mathrm{V\,(aq;\, w_1 = 1\ kg)}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

Hence,

$$\mathrm{K_T\,(aq;\, w_1 = 1\ kg)} = \mathrm{M_1^{-1}}\,\mathrm{K_{T1}^*}(\ell) + \mathrm{m_j}\,\phi\,(\mathrm{K_{Tj}})$$

Moreover recalling that $\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\phi\,(\mathrm{V_j}) = \phi\,(\mathrm{V_j})^{\infty} = \mathrm{V_j^{\infty}(aq)}$,

$$\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\phi\left(\mathrm{K_{T_j}}\right) = \phi\left(\mathrm{K_{T_j}}\right)^{\infty} = \mathrm{K_{T_j}^{\infty}(aq)}$$

These equations combined with those yielding $\phi\left(\mathrm{K_{T_j}}\right)$ from measured $\kappa_{\mathrm{T1}}^*(\ell)$ and $\kappa_{\mathrm{T}}\mathrm{(aq)}$ signal an attractive approach to the study of solvent-solute interactions via $\mathrm{K_{T_j}^{\infty}(aq)}$. In this context Gurney [4] identified a cosphere of solvent around a solute molecule where the organization differs from that in the bulk solvent at some distance from a given solute molecule j. For example, the limiting partial molar volume of solute j can be understood as the sum of two terms, V(intrinsic) and V(cosphere). Then V (cosphere) is an indicator of the role of solvent-solute interaction, hydration in aqueous solution. Thus,

$$V_j^{\infty}(aq) = V_j\ (\mathrm{int\ rinsic}\ ) + V_j(\mathrm{cos}\,phere)$$

Hence,

$$\mathrm{K_{T_j}^{\infty}(aq)} = \mathrm{K_{T_j}}\ (\mathrm{int\ rinsic})\ + \mathrm{K_{T_j}(cos\,phere)}$$

The argument is advanced that $\mathrm{K_{Tj}}$(intrinsic) for simple ions such as halide ions and alkali metal ions is zero. $\mathrm{K_{T_j}^{\infty}(aq)}$ is an indicator of the hydration of a given solute in aqueous solution. $\mathrm{K_{T_j}^{\infty}(aq)}$ is obtained from the dependence of $\phi\left(\mathrm{K_{T_j}}\right)$ on, for example, concentration c_j using equation(l) for neutral solutes and equation (m) for salts, the latter being based on the DHLL.

$$\phi\left(\mathrm{K_{T_j}}\right) = \mathrm{K^{\infty}_{T_j}(aq)} + \mathrm{a_{KT}}\ \left(\mathrm{c_j/c_r}\right)$$

$$\phi\left(\mathrm{K_{T_j}}\right) = \mathrm{K^{\infty}_{T_j}(aq)} + \mathrm{b_{KT}}\ \left(\mathrm{c_j/c_r}\right)^{1/2}$$

One might have expected an extensive scientific literature reporting $\mathrm{K^{\infty}_{T_j}(aq)}$ for a wide range of solutes. Unfortunately measurement of isothermal compressions of liquids is difficult at least to the precision required for the estimation of $\mathrm{K^{\infty}_{Tj}(aq)}$. Indeed direct measurement of the volume change of a liquid when compressed at constant temperature is difficult because the isothermal condition is difficult to satisfy. Two procedures have been adopted to over come this problem. In both cases isentropic compressibilities calculated from densities and speeds of sound have been used.

In one set of procedures, isentropic compressibilities, densities and isobaric heat capacities are used to calculate isothermal compressions for a given solution, molality m_j. For example, Bernal and Van Hook [5] use the Desnoyers-Philip Equation to evaluate $\phi\left(K_{T_j}\right)^{\infty}$ for glucose, sucrose and fructose [5] in aqueous solutions at $348\ \mathrm{K}$. An alternative procedure equates $\phi\left(\mathrm{K_{Tj}}\right)^{\infty}$ with the experimentally accessible limiting apparent isentropic compression, ∞ φ(K) Sj . In another approach, the starting point is equation (a) which is differentiated with respect to pressure at constant temperature to yield equation (n).

$$\mathrm{K_T(aq)} = \mathrm{n_1\,K_{Tl}(aq)} + \mathrm{n_j\,K_{T_j}(aq)}$$

Equation (n) is divided by volume $\mathrm{V(aq)}$. Hence

$$\mathrm{K_T(aq)/V(aq)} = \left[\mathrm{n_1\,V_1(aq)/V(aq)}\right]\ \left[1/\mathrm{V_1(aq)}\right]\ \mathrm{K_1(aq)} + \left[\mathrm{n_j\,V_j(aq)/V(aq)}\right]\ \left[1/\mathrm{V_j(aq)}\right]\ \mathrm{K_j(aq)}$$

We use $\phi_1\ [= \mathrm{n_1\,V_1(aq)/V(aq)}]$ and $\phi_j\ [= \mathrm{n_j\,V_j(aq)/V(aq)}]$ to express volume fractions.

$$\kappa_T\mathrm{(aq)} = \phi_1\ \left[1/\mathrm{V_1(aq)}\right]\ \mathrm{K_{T1}(aq)} + \phi_j\ \left[1/\mathrm{V_j(aq)}\right]\ \mathrm{K_{Tj}(aq)}$$

The latter equation is not tremendously helpful. Although $\kappa_T\mathrm{(aq)}$ can be measured, the right hand side involves six terms about which we have no information ‘a priori’ and which depend on the composition of the solution.

Footnotes

[1] F. T. Gucker, Chem. Rev.,1933,**14**,127.

[2] F. T. Gucker, J. Am. Chem. Soc.,1933, **55**,2709.

[3] Units; $\phi\left(\mathrm{K_{Tj}}\right) = \left[\mathrm{m^3\ mol^{-1}\ Pa^{-1}}\right]$; $\mathrm{K^*_{T1}}(\ell) = \left[\mathrm{m^3\ mol^{-1}\ Pa^{-1}}\right]$; $\mathrm{K_T(aq)} = \left[\mathrm{m^3\ Pa^{-1}}\right]$

For the solution $\kappa_T\mathrm{(aq)} = \mathrm{K_T(aq)/V(aq)} = \left[\mathrm{Pa^{-1}}\right]$

For the solvent $\kappa^*_{T1}(\ell) = \mathrm{K^*_{T1}}(\ell)/\mathrm{V^*_1}(\ell) = \left[\mathrm{Pa^{-1}}\right]$

Isothermal compressions have units of ‘volume per unit of pressure’ whereas compressibilities have units of ‘reciprocal pressure’. $\phi\left(\mathrm{K_{T_j}}\right)$ is an apparent molar isothermal compression on the grounds that the units of this quantity are $\left[\mathrm{m^3\ mol^{-1}\ Pa^{-1}}\right]$. Some reports use the term ‘apparent molar isothermal compressibility’ which should be avoided because in the present context this term corresponds to a different property; see J. C. R. Reis, J. Chem. Soc. Faraday Trans.,1998,**94**,2385.

[4] R.W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.

[5] P. D. Bernal and W. A. Van Hook, J. Chem. Thermodyn., 1986,**18**,955.

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1.7.19: Compressions- Isothermal- Solutions- Apparent Molar- Determination

A given solution (at fixed T and p) is prepared using $1\ \mathrm{kg}$ of solvent water and m_j moles of solute j. The compression of this solution $\mathrm{K_T\,(aq;w_1 = 1\ kg)}$ is given by equations (a) and (b).

$$\mathrm{K_T\,(aq;w_1 = 1\ kg) = M_1^{-1}\,K_{T1}^{*}(\ell) + m_j\,\phi\,(K_{T_j})}$$

$$\mathrm{K_T\,(aq;w_1 = 1\ kg) = M_1^{-1}\,K_{T1}(aq) + m_j\,K_{Tj}(aq)}$$

where,

$$\mathrm{K_{T_j}(aq) = -\left(\frac{\partial V_j}{\partial p}\right)_T}$$

and

$$\mathrm{\phi\,(K_{T_j}) = -\left(\frac{\partial \phi\,(V_j)}{\partial p}\right)_T}$$

Both $\mathrm{K_{Tj}(aq)}$ and $\mathrm{\phi\,(K_{Tj})}$ are Lewisian variables. With reference to partial molar volumes,

$$\mathrm{limit\,(m_j \to 0)\,\phi\,(V_j) = \phi\,(V_j)^{\infty} = V_j^{\infty}(aq)}$$

Hence

$$\mathrm{limit\,(m_j \to 0)\,\phi\,(K_{T_j}) = \phi\,(K_{T_j})^{\infty} = K_{T_j}^{\infty}(aq)}$$

$\mathrm{\phi\,(K_{T_j})^{\infty}}$ is the limiting (infinite dilution) apparent molar compression of solute--j. For a given solution $\mathrm{\phi\,(K_{T_j})}$ is calculated using one of the following equations together with the isothermal compressions of solution and solvent [1-3].

Molality Scale

$$\mathrm{\phi\,(K_{T_j}) = [m_j\,\rho_1^{*}(\ell)]^{-1}\,[\kappa_T(aq) - \kappa_{T1}^{*}(\ell)] + \kappa_T(aq)\,\phi\,(V_j)}$$

$$\mathrm{\phi\,(K_{T_j}) = [m_j\,\rho(aq)\,\rho_1^{*}(\ell)]^{-1}\,[\kappa_T(aq)\,\rho_1^{*}(\ell) - \kappa_{T1}^{*}(\ell)\,\rho(aq)] + \kappa_T(aq)\,M_j\,[\rho(aq)]^{-1}}$$

Concentration Scale

$$\mathrm{\phi\,(K_{TJ}) = [c_j\,\rho_1^{*}(\ell)]^{-1}\,[\kappa_T(aq)\,\rho_1^{*}(\ell) - \kappa_{T1}^{*}(\ell)\,\rho(aq)] + \kappa_{T1}^{*}(\ell)\,M_j/\rho_1^{*}(\ell)}$$

Also

$$\mathrm{\phi\,(K_{T_j}) = [c_j]^{-1}\,[\kappa_T(aq) - \kappa_{Tl}^{*}(\ell)] + \kappa_{T1}^{*}(\ell)\,\phi\,(V_j)}$$

The latter four equations are thermodynamically correct, no assumption being made in their derivation.

In 1933, Gucker reviewed the direct determination of compressibilities of solutions leading to apparent molar compressions of solutes in aqueous solution calculated using equation (k) [4-6].

$$\mathrm{\phi\,(K_{T_j}) = \frac{\kappa_T(aq)}{\rho(aq)}\left[\frac{1}{m_j} + M_j\right] - \frac{\kappa_1^{*}(\ell)}{\rho_1^{*}(\ell)}\frac{1}{m_j}}$$

Compressibilties of solutions were directly determined by measuring the sensitivity of $\mathrm{V(aq)}$ to an increase in pressure. Gucker showed that for aqueous salt solutions, $\mathrm{\phi\,(K_{T_j})}$ is negative and a linear function of $\mathrm{(c_j)^{1/2}}$. Moreover the limiting value, $\mathrm{\phi\,(K_{T_j})^{\infty}}$ is an additive property of $\mathrm{\phi\,(K_T - 1ion)^{\infty}}$

A useful approximation is that for dilute solutions at constant T and p containing a neutral solute j, $\mathrm{\phi\,(K_{T_j})}$ is linear function of molaity m_j.

$$\mathrm{\phi\,(K_{T_j}) = e\,m_j + f}$$

Hence,

$$\text{limit}\,(\mathrm{m_j} \rightarrow 0)\,\mathrm{K_{T_j}(aq)} = \mathrm{K_{Tj}^{\infty}(aq)} = \phi\left(\mathrm{K_{T_j}}\right)^{\infty}$$

We identify 'f' in equation (l) as the limiting isothermal apparent molar isothermal compression of solute j in solution (at equilibrium).

Footnotes

[1] $\phi\left(\mathrm{K_{Tj}}\right) = \left[\mathrm{m^3\ mol^{-1}\ Pa^{-1}}\right]; \mathrm{K_{Tl}^{*}} = \left[\mathrm{m^3\ mol^{-1}\ Pa^{-1}}\right]; \mathrm{K_T(aq)} = \left[\mathrm{m^3\ Pa^{-1}}\right]$

For the solution, $\kappa_{\mathrm{T}} = \mathrm{K_T(aq)/V(aq)} = \left[\mathrm{Pa^{-1}}\right]$

For the solvent, $\kappa_{\mathrm{T1}}^{*}(\ell) = \mathrm{K_{T1}^{*}}(\ell)/\mathrm{V_1^{*}}(\ell) = \left[\mathrm{Pa^{-1}}\right]$

[2] Isothermal compressions have units 'volume per unit of pressure' whereas compressibilities have units of 'reciprocal pressure'. $\phi\left(\mathrm{K_{T_j}}\right)$ is an apparent molar isothermal compression on the grounds that the units of this property are $\left[\mathrm{m^3\ mol^{-1}\ Pa^{-1}}\right]$. Some reports use the term 'apparent molar isothermal compressibility'.

[3] For an aqueous solution at fixed temperature and pressure prepared using $\mathrm{n_1}$ moles of water and n_j moles of solute j,

$$\mathrm{V(aq)} = \mathrm{n_1\,V_1^{*}}(\ell) + \mathrm{n_j}\,\phi\left(\mathrm{V_j}\right)$$

Hence with respect to an equilibrium displacement (i.e. at $\mathrm{A} = 0$) at defined temperature,

$$\left(\partial \mathrm{V(aq)}/\partial \mathrm{p}\right)_{\mathrm{T}} = \mathrm{n_1}\,\left(\partial \mathrm{V_1^{*}}(\ell)/\partial \mathrm{p}\right)_{\mathrm{T}} + \mathrm{n_j}\,\left(\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{p}\right)_{\mathrm{T}}$$

Hence

$$\left(\partial \mathrm{V(aq)}/\partial \rho\right)_{\mathrm{T}} = \mathrm{n_1}\,\left(\partial \mathrm{V_1^{*}}(\ell)/\partial \mathrm{p}\right)_{\mathrm{T}} - \mathrm{n_j}\,\phi\left(\mathrm{K_{T_j}}\right)$$

For the solution the (equilibrium) isothermal compressibility,

$$\kappa_{\mathrm{T}}(\mathrm{aq}) = -\frac{1}{\mathrm{V(aq)}}\left(\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

Similarly for the pure solvent,

$$\kappa_{\mathrm{T1}}^{*}(\ell) = -\frac{1}{\mathrm{V_1^{*}}(\ell)}\left(\frac{\partial \mathrm{V_1^{*}}(\ell)}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

Hence from equation (c),

$$\mathrm{V(aq)\,K_T(aq)} = \mathrm{n_1\,V_1^{*}}(\ell)\,\mathrm{K_{T1}^{*}}(\ell) + \mathrm{n_j}\,\phi\left(\mathrm{K_{Tj}}\right)$$

We use equation (as) for $\mathrm{V(aq)}$ in conjunction with equation (f).

$$\kappa_{\mathrm{T}}(\mathrm{aq})\ \left[\mathrm{n_1\,V_1^{*}}(\ell) + \mathrm{n_j}\,\phi\left(\mathrm{V_j}\right)\right] = \mathrm{n_1\,V_1^{*}}(\ell)\,\mathrm{K_{T1}^{*}}(\ell) + \mathrm{n_j}\,\phi\left(\mathrm{K_{T_j}}\right)$$

$$\phi\left(\mathrm{K_{Tj}}\right) = \left[\kappa_{\mathrm{T}}(\mathrm{aq})\,\mathrm{n_1\,V_1^{*}}(\ell)\right]/\mathrm{n_j} - \left[\mathrm{n_1\,V_1^{*}}(\ell)\,\mathrm{K_{T1}^{*}}(\ell)/\mathrm{n_j}\right] + \phi\left(\mathrm{V_j}\right)\,\kappa_{\mathrm{T}}(\mathrm{aq})$$

But, $\mathrm{V_1^{*}}(\ell) = \mathrm{M_1}/\rho_1^{*}(\ell)$ Then,

$$\phi\left(\mathrm{K_{T_j}}\right) = \kappa_{\mathrm{T}}(\mathrm{aq})\,\frac{\mathrm{n_1\,M_1}}{\rho_1^{*}(\ell)\,\mathrm{n_j}} - \frac{\mathrm{n_1\,M_1}}{\rho_1^{*}(\ell)\,\mathrm{n_j}}\,\mathrm{K_{T1}^{*}}(\ell) + \phi\left(\mathrm{V_j}\right)\,\mathrm{K_T(aq)}$$

$\mathrm{m_j} = \mathrm{n_j}/\mathrm{n_l}\,\mathrm{M_l}$

Molality $\phi\left(\mathrm{K_{Tj}}\right) = \dfrac{\kappa_{\mathrm{T}}(\mathrm{aq})}{\mathrm{m_j}\,\rho_1^{*}(\ell)} - \dfrac{\kappa_{\mathrm{T1}}^{*}(\ell)}{\rho_1^{*}(\ell)\,\mathrm{m_j}} + \phi\left(\mathrm{V_j}\right)\,\kappa_{\mathrm{T}}(\mathrm{aq})$

Or,

$$\phi\left(\mathrm{K_{TJ}}\right) = \left[\mathrm{m_j}\,\rho_1^{*}(\ell)\right]^{-1}\,\left[\kappa_{\mathrm{T}}(\mathrm{aq}) - \kappa_{\mathrm{T1}}^{*}(\ell)\right] + \phi\left(\mathrm{V_j}\right)\,\kappa_{\mathrm{T}}(\mathrm{aq})$$

Using again equation (a) to substitute for $\phi\left(\mathrm{V_j}\right)$,

$$\phi\left(\mathrm{K_{T_j}}\right) = \left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\left[\kappa_\mathrm{T}(\mathrm{aq}) - \kappa_{\mathrm{T1}}^*(\ell)\right] + \kappa_\mathrm{T}(\mathrm{aq})\left[\frac{\mathrm{V(aq)} - \mathrm{n_1}\,\mathrm{V_1^*}(\ell)}{\mathrm{n_j}}\right]$$

With $\mathrm{c_j} = \mathrm{n_j}/\mathrm{V(aq)}$,

$$\phi\left(\mathrm{K_{T_j}}\right) = \left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\left[\kappa_\mathrm{T}(\mathrm{aq}) - \kappa_{\mathrm{T1}}^*(\ell)\right] + \kappa_\mathrm{T}(\mathrm{aq})\left[\frac{1}{\mathrm{c_j}} - \frac{\mathrm{n_1}\,\mathrm{M_1}}{\rho_1^*(\ell)\,\mathrm{n_j}}\right]$$

But $\frac{1}{c_j} = \frac{M_j}{\rho(aq)} + \frac{1}{m_j\,\rho(aq)}$ Hence,

$$\phi\left(\mathrm{K_{T_j}}\right) = \left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\left[\kappa_\mathrm{T}(\mathrm{aq}) - \kappa_{\mathrm{Tl}}^*(\ell)\right] + \kappa_\mathrm{T}(\mathrm{aq})\left[\frac{\mathrm{M_j}}{\rho(\mathrm{aq})} + \frac{1}{\mathrm{m_j}\,\rho(\mathrm{aq})} - \frac{\mathrm{n_1}\,\mathrm{M_1}}{\rho_1^*(\ell)\,\mathrm{n_j}}\right]$$

$$\phi\left(\mathrm{K_{T_j}}\right) = \left[\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_1^*(\ell)\right]^{-1}\left[\kappa_\mathrm{T}(\mathrm{aq})\,\rho_1^*(\ell) - \kappa_{\mathrm{T1}}^*(\ell)\,\rho(\mathrm{aq})\right] + \frac{\kappa_\mathrm{T}(\mathrm{aq})\,\mathrm{M_j}}{\rho(\mathrm{aq})}$$

We start with equation (f).

$$\mathrm{V(aq)}\,\mathrm{K_T(aq)} = \mathrm{n_1}\,\mathrm{V_1^*}(\ell)\,\kappa_{\mathrm{T1}}^*(\ell) + \mathrm{n_j}\,\phi\left(\mathrm{K_{T_j}}\right)$$

Mass of solution,

$$V(aq)\,\rho(aq) = n_1\,M_1 + n_j\,M_j$$

Or,

$$\mathrm{n_1} = \left[\mathrm{V(aq)}\,\rho(\mathrm{aq}) - \mathrm{n_j}\,\mathrm{M_j}\right]/\mathrm{M_1}$$

We combine equations (f) and (q).

$$\mathrm{V(aq)}\,\kappa_\mathrm{T}(\mathrm{aq}) = \mathrm{V_1^*}(\ell)\,\kappa_{\mathrm{T1}}^*(\ell)\left[\frac{\mathrm{V(aq)}\,\rho(\mathrm{aq}) - \mathrm{n_j}\,\mathrm{M_j}}{\mathrm{M_1}}\right] + \mathrm{n_j}\,\phi\left(\mathrm{K_{T_j}}\right)$$

With $c_j = n_j/V(aq)$

$$\phi\left(\mathrm{K_{T_j}}\right) = \frac{\kappa_\mathrm{T}(\mathrm{aq})}{\mathrm{c_j}} - \frac{\mathrm{V_1^*}(\ell)\,\kappa_{\mathrm{T1}}^*(\ell)\,\rho(\mathrm{aq})}{\mathrm{c_j}\,\mathrm{M_1}} + \frac{\mathrm{V_1^*}(\ell)\,\kappa_{\mathrm{T1}}^*(\ell)\,\mathrm{M_j}}{\mathrm{M_1}}$$

Hence,

$$\phi\left(\mathrm{K_{Tj}}\right) = \left[\mathrm{c_j}\,\rho_1^*(\ell)\right]^{-1}\left[\kappa_\mathrm{T}(\mathrm{aq})\,\rho_1^*(\ell) - \kappa_{\mathrm{T1}}^*(\ell)\,\rho(\mathrm{aq})\right] + \kappa_{\mathrm{Tl}}^*(\ell)\,\mathrm{M_j}/\rho_1^*(\ell)$$

Again from equation (j)

$$\phi\left(\mathrm{K_{T_j}}\right) = \left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\left[\mathrm{K_T(aq)} - \kappa_{\mathrm{T1}}^*(\ell)\right] + \phi\left(\mathrm{V_j}\right)\,\kappa_\mathrm{T}(\mathrm{aq})$$

Hence,

$$\phi\left(\mathrm{K_{T_j}}\right) = \left[\frac{\rho_1^*(\ell)}{\mathrm{c_j}} - \phi\left(\mathrm{V_j}\right)\,\rho_1^*(\ell)\right]\left[\rho_1^*(\ell)\right]^{-1}\left[\kappa_\mathrm{T}(\mathrm{aq}) - \kappa_{\mathrm{T1}}^*(\ell)\right] + \phi\left(\mathrm{V_j}\right)\,\kappa_\mathrm{T}(\mathrm{aq})$$

Or

$$\phi\left(\mathrm{K_{Tj}}\right) = \left[\mathrm{c_j}\right]^{-1}\left[\mathrm{K_T(aq)} - \kappa_{\mathrm{T1}}^*(\ell)\right] + \phi\left(\mathrm{V_j}\right)\,\kappa_{\mathrm{T1}}^*(\ell)$$

[4] F. T. Gucker, J.Am.Chem.Soc.,1933,**55**,2709.

[5] F. T. Gucker, Chem. Rev.,1933,**13**,111.

[6] From equation (h),

$$\phi\left(\mathrm{K}_{\mathrm{T}_{\mathrm{j}}}\right)=\frac{\kappa_{\mathrm{T}}(\mathrm{aq})\,\rho_{1}^{*}(\ell)}{\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_{1}^{*}(\ell)}-\frac{\kappa_{\mathrm{T}1}^{*}(\ell)\,\rho(\mathrm{aq})}{\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_{1}^{*}(\ell)}+\frac{\kappa_{\mathrm{T}}(\mathrm{aq})\,\mathrm{M_j}}{\rho(\mathrm{aq})}$$

$$\phi\left(\mathrm{K_T}\right)=\frac{\kappa_{\mathrm{T}}(\mathrm{aq})}{\rho(\mathrm{aq})}\left[\frac{1}{\mathrm{m_j}}+\mathrm{M_j}\right]-\frac{\kappa_{\mathrm{T}1}^{*}(\ell)}{\mathrm{m_j}\,\rho_{1}^{\star}(\ell)}$$

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1.7.20: Compressions- Isothermal- Salt Solutions

In 1933 Gucker [1-3] reviewed attempts to measure the apparent isothermal molar compressions of salts in aqueous solution, these attempts dating back to the earliest reliable measurements by Rontgen and Schneider [4] in 1886 and 1887. Gucker showed [2] that for several aqueous salt solutions the apparent isothermal molar compression, $\phi\left(\mathrm{K_{T_j}}\right)$ is a linear function of the square root of the salt concentration.

$$\phi\left(\mathrm{K_{T_j}}\right) = \phi\left(\mathrm{K_{T_j}}\right)^{\infty} + \mathrm{a\, c_j^{1/2}}$$

This general equation holds for $\mathrm{CaCl_2(aq)}$ at 60 Celsius. In general terms, $\phi\left(\mathrm{K_{T_j}}\right)$ for salts is negative becoming less negative as the salt concentration increases. Gibson described an interesting approach which characterises salt solutions in terms of effective pressures, $\mathrm{p_c}$ exerted by the salt on the solvent [5]. This effective pressure is expressed as a linear function of the product of salt and solvent concentrations. The constant of proportionality is characteristic of the salt. Leyendekkers based an analysis using the Tammann-Tait-Gibson (TTG) model, on the assertion that solutes, salts and organic solutes, exert an excess pressure on water in aqueous solution [6,7]. The TTG approach described by Leyendekkers is intuitively attractive but the analysis is based on an extra - thermodynamic assumption [8]. Calculation of an excess pressure requires an estimate of the volume of solute molecules, ϕ_j in solution. If this property is independent of solute molality m_j, the dependence of the volume of a solution (in $1\ \mathrm{kg}$ of water) on solute molality is described by the dependence of the 'partial molar volume' of water. The difference between $[\mathrm{V\,(aq;\, w_1 = 1\ kg) - m_j\,\phi(Vj)}]$ and $\mathrm{M_1^{-1}\ V_1^*(\ell)}$ is understood in terms of an effective pressure on the solvent. The assumptions underlying this calculation are not trivial. Furthermore from a thermodynamic viewpoint, the pressure is the same in every volume element of a solution [8].

Footnotes

[1] F. T. Gucker, J. Am. Chem.Soc.,1933,**55**,2709.

[2] F. T. Gucker, Chem.Rev.,1933,**13**,111.

[3] F. T. Gucker, F. W. Lamb, G. A. Marsh and R. M. Haag, J.Am. Chem. Soc.,1950,**72**,310.

[4] W. C. Rontgen and J. Schneider, Wied. Ann., 1886,**29**,165;1887,**31**,36.

[5] R. E. Gibson, J.Am.Chem.Soc.,1934,**56**,4.;1935,**57**,284.

[6] J. V. Leyendekkers, J. Chem. Soc. Faraday Trans.1,1981,**77**,1529; 1982,**78**,357; 1988,**84**, 397,1653.

[7] J. V. Leyendekkers, Aust. J. Chem.,1981,**34**,1785.

[8] M. J. Blandamer, J. Burgess and A. Hakin, J. Chem. Soc. Faraday Trans.1,1986, **82**,3681.

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1.7.21: Compressions- Isothermal- Binary Aqueous Mixtures

A given binary aqueous mixture is prepared using n_1 moles of water (ℓ) and n_2 moles of liquid 2. The volume of the mixture, $\mathrm{V(mix)}$ is given by equation (a) (at fixed temperature and pressure).

$$\mathrm{V(mix) = n_1\, V_1(mix) + n_2\, V_2(mix)}$$

The mixture is perturbed by a change in pressure at fixed temperature along an equilibrium pathway where the affinity for spontaneous change remains at zero.

$$\left(\frac{\partial \mathrm{V(mix)}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \mathrm{n_1}\left(\frac{\partial \mathrm{V_1(mix)}}{\partial \mathrm{p}}\right)_{\mathrm{T}} + \mathrm{n_2}\left(\frac{\partial \mathrm{V_2(mix)}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

The isothermal compression of the mixture $[\partial \mathrm{V(mix)}/\partial \mathrm{p}]_{\mathrm{T}}$ is an extensive property. The partial differentials $[\partial V_1(\mathrm{mix})/\partial p]_T$ and $[\partial V_2(\mathrm{mix})/\partial \mathrm{p}]_{\mathrm{T}}$ are intensive properties. There is merit in defining an intensive molar compression using equation (c).

$$\mathrm{K_{Tm}} = \frac{\mathrm{K_T(mix)}}{(\mathrm{n_1 + n_2})} = -\,(\mathrm{n_1 + n_2})^{-1}\,[\partial \mathrm{V(mix)}/\partial \mathrm{p}]_{\mathrm{T}}$$

By definition,

$$\mathrm{K_{T1}(mix)} = -\,[\partial \mathrm{V_1(mix)}/\partial \mathrm{p}]_{\mathrm{T}}$$

And

$$\mathrm{K_{T2}(mix)} = -\,[\partial \mathrm{V_2(mix)}/\partial \mathrm{p}]_{\mathrm{T}}$$

Hence

$$\mathrm{K_{Tm}(mix) = x_1\, K_{T1}(mix) + x_2\, K_{T2}(mix)}$$

For an ideal binary mixture,

$$\mathrm{V(mix; id) = n_1\, V_1^*(\ell) + n_2\, V_2^*(\ell)}$$

$\mathrm{V_1^*(\ell)}$ and $\mathrm{V_2^*(\ell)}$ are the molar volumes of the pure liquids at the same T and p. Therefore, following the argument outlined above,

$$\mathrm{K_{Tm}(id) = x_1\, K_{T1}^*(\ell) + x_2\, K_{T2}^*(\ell)}$$

By definition,

$$\mathrm{K_T^E(mix) = K_{Tm}(mix) - K_{Tm}(mix; id)}$$

Hence the excess molar compression is given by equation (j).

$$\mathrm{K_{Tm}^E(mix) = x_1\,[K_{T1}(mix) - K_{T1}^*(\ell)] + x_2\,[K_{T2}(mix) - K_{T2}^*(\ell)]}$$

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1.7.22: Compressions- Isothermal- Liquid Mixtures Binary- Compressibilities

The isothermal compressibility of a given binary liquid mixture having ideal thermodynamic properties is related to the isothermal compressions of the liquid components using equation (a) [1].

$$\mathrm{K_T(mix;id)} = \frac{\mathrm{K^*_{T1}}(\ell) + \mathrm{x_2}\ [\mathrm{K^*_{T2}}(\ell) - \mathrm{K^*_{T1}}(\ell)]}{\mathrm{V^*_1}(\ell) + \mathrm{x_2}\ [\mathrm{V^*_2}(\ell) - \mathrm{V^*_1}(\ell)]}$$

The excess compression for a given binary liquid mixture is defined by equation (b).

$$\mathrm{K^E_{Tm}} = \mathrm{K_{Tm}(mix)} - \mathrm{K_{Tn}(mix;id)}$$

Or,

$$\mathrm{K^E_{Tm}} = \mathrm{K_{Tm}(mix)} - [\mathrm{x_1\,K^*_{T1}}(\ell) + \mathrm{x_2\,K^*_{T2}}(\ell)]$$

The isothermal compressibilities of ideal and real binary liquid mixtures are defined by equations (d) and (e) respectively.

$$\kappa_\mathrm{T}(\mathrm{mix;id}) = -\frac{1}{\mathrm{V(mix;id)}}\left(\frac{\partial \mathrm{V(mix;id)}}{\partial \mathrm{p}}\right)_\mathrm{T}$$

$$\kappa_\mathrm{T}(\mathrm{mix}) = -\frac{1}{\mathrm{V(mix)}}\left(\frac{\partial \mathrm{V(mix)}}{\partial \mathrm{p}}\right)_\mathrm{T}$$

For a given binary liquid mixture we can define an excess compressibility using equation (f).

$$\kappa^\mathrm{E}_\mathrm{T} = \kappa_\mathrm{T}(\mathrm{mix}) - \kappa_\mathrm{T}(\mathrm{mix;id})$$

Then

$$\kappa^\mathrm{E}_\mathrm{T}(\mathrm{mix}) = -\frac{1}{\mathrm{V(mix)}}\left(\frac{\partial \mathrm{V(mix)}}{\partial \mathrm{p}}\right)_\mathrm{T} + \frac{1}{[\mathrm{x_1\,V^*_1}(\ell) + \mathrm{x_2\,V^*_2}(\ell)]}\left(\frac{\partial\,[\mathrm{x_1\,V^*_1}(\ell) + \mathrm{x_2\,V^*_2}(\ell)]}{\partial \mathrm{p}}\right)_\mathrm{T}$$

A similar equation was used by Moelwyn-Hughes and Thorpe [3]. They introduced the concept of a compressibility of the excess volume.

$$\Delta\kappa_\mathrm{T}(\mathrm{mix}) = -\frac{1}{\Delta\mathrm{V(mix)}}\left(\frac{\partial \Delta\mathrm{V(mix)}}{\partial \mathrm{p}}\right)_\mathrm{T}$$

In publications by Prigogine and by Moelwyn-Hughes and Thorpe the analysis was taken a step further to facilitate analysis of experimental results. However approximations were made in both treatments. An exact formulation was given by Missen [4] in terms of volume fractions of both components in the corresponding having ideal thermodynamic properties, $\phi_1(\ \mathrm{mix;id}\ )$ and $\phi_2(\ \mathrm{mix;id}\ )$. Hence,

$$\kappa^\mathrm{E}_\mathrm{T}(\mathrm{mix}) = -\frac{1}{\mathrm{V_m(mix)}}\left[\left(\frac{\partial \mathrm{V^E_m}}{\partial \mathrm{p}}\right)_\mathrm{T} + \mathrm{V^E_m}\,\kappa_\mathrm{T}(\mathrm{mix;id})\right]$$

A partial compressibility was defined by Moelwyn-Hughes [5]. For liquid 1 in a binary liquid mixture at defined T and p, the partial compressibility is defined by equation (j).

$$\kappa_{T_1}(\mathrm{mix}) = -\frac{1}{V_1(\mathrm{mix})}\left(\frac{\partial V_1(\mathrm{mix})}{\partial p}\right)_T$$

Similarly for component 2,

$$\kappa_{\mathrm{T}2}(\mathrm{mix}) = -\frac{1}{\mathrm{V}_2(\mathrm{mix})}\left(\frac{\partial \mathrm{V}_2(\mathrm{mix})}{\partial \mathrm{p}}\right)_\mathrm{T}$$

The excess compressibility of a given binary liquid mixture $\mathrm{K^E_T(mix)}$ was defined in equation (f). Hence,

$$\kappa_{\mathrm{T}}^{\mathrm{E}}(\mathrm{mix}) = \phi_1(\mathrm{mix})\,\kappa_{\mathrm{T1}}^{\mathrm{E}}(\mathrm{mix}) + \phi_2(\mathrm{mix})\,\kappa_{\mathrm{T2}}^{\mathrm{E}}(\mathrm{mix}) + [\phi_1(\mathrm{mix}) - \phi_1(\mathrm{mix};\mathrm{id})]\,\kappa_{\mathrm{T1}}^{*}(\ell) + [\phi_2(\mathrm{mix}) - \phi_2(\mathrm{mix};\mathrm{id})]\,\kappa_{\mathrm{T2}}^{*}(\ell)$$

It may be noted that 'true' partial properties can also be defined for the isothermal compressibility [6]. Then the properties introduced in equations (j) and (k) would be termed specific partial isothermal compressions [6].

It is also possible to formulate a set of equations incorporating rational activity coefficients for the two components of the binary liquid mixture. We start with the equation for the partial molar volume of component 1.

$$V_1(\mathrm{mix}) = V_1^*(\ell) + RT\left(\frac{\partial \ln(f_1)}{\partial p}\right)_T$$

$$K_{T1}(\mathrm{mix}) = K_{T1}^*(\ell) - RT\left(\frac{\partial^2 \ln(f_1)}{\partial p^2}\right)_T$$

Similarly

$$\mathrm{K_{T2}(mix) = K_{T2}^*(\ell) - R\,T\left(\frac{\partial^2 \ln(f_2)}{\partial p^2}\right)_T}$$

Therefore

$$\mathrm{K_{Tm}(mix) = K_{Tm}(mix;id) - R\,T\left[x_1\left(\frac{\partial^2 \ln(f_1)}{\partial p^2}\right)_T + x_2\left(\frac{\partial^2 \ln(f_2)}{\partial p^2}\right)_T\right]}$$

The two liquid components are characterised by their molar excess properties.

$$\mathrm{K_{T1}^E(mix) = -R\,T\left(\frac{\partial^2 \ln(f_1)}{\partial p^2}\right)_T}$$

and

$$\mathrm{K_{T2}^E(mix) = -R\,T\left(\frac{\partial^2 \ln(f_2)}{\partial p^2}\right)_T}$$

Therefore

$$\mathrm{K_{Tm}^E(mix) = -R\,T\left[x_1\left(\frac{\partial^2 \ln(f_1)}{\partial p^2}\right)_T + x_2\left(\frac{\partial^2 \ln(f_2)}{\partial p^2}\right)_T\right]}$$

Also

$$\mathrm{K_{T1}^E = -\left(\frac{\partial V_1^E}{\partial p}\right)_T \text{ and } K_{T2}^E = -\left(\frac{\partial V_2^E}{\partial p}\right)_T}$$

In other words

$$\mathrm{K_{Tm}^E = -\left(\frac{\partial V_m^E}{\partial p}\right)_T}$$

Isothermal compressions of liquid mixtures can be directly measured [7]. Hamann and Smith [8] report measurements using binary liquid mixtures at 303 K and two pressures. Hamann and Smith define excess isothermal molar compressions $\mathrm{K_T^E}(\phi)$ in terms of volume fraction weighted isothermal compressions of the pure liquids. The volume fractions are defined as follows.

$$\phi_1 = \mathrm{x_1\,V_1^*(\ell)/\left[x_1\,V_1^*(\ell) + x_2\,V_2^*(\ell)\right]}$$

$$\phi_2 = x_2\,V_2^*(\ell)/\left[x_1\,V_1^*(\ell) + x_2\,V_2^*(\ell)\right]$$

Then

$$\mathrm{K_T^E}(\phi) = \mathrm{K_{Tm}(mix) - [\phi_1\,K_{T1}^*(\ell) + \phi_2\,K_{T2}^*(\ell)]}$$

For most binary aqueous mixtures $\mathrm{K_T^E}(\phi)$ is negative, plots of $\mathrm{K_T^E}(\phi)$ against ϕ_2 being smooth curves. The minima in aqueous mixtures containing THF and propanone the minima are near 0.4 and 0.6 respectively [0].

Footnotes

[1] For a binary liquid mixture having ideal thermodynamic properties,

$$V_m(\text{mix; id}) = x_1 V_1^*(\ell) + x_2 V_2^*(\ell)$$

Then

$$K_{Tm}(\text{mix; id}) = x_1 K_{T1}^*(\ell) + x_2 K_{T2}^*(\ell)$$

But

$$\kappa_T(\text{mix; id}) = \frac{K_{Tm}(\text{mix; id})}{V_m(\text{mix; id})}$$

Then,

$$\kappa_T(\text{mix; id}) = \frac{K_{T1}^*(\ell) + x_2\ [K_{T2}^*(\ell) - K_{T1}^*(\ell)]}{V_1^*(\ell) + x_2\ [V_2^*(\ell) - V_1^*(\ell)]}$$

[2] I. Prigogine, The Molecular Theory of Solutions, North Holland, Amsterdam, 1957, p.18.

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[4] R. W. Missen, Ind. Eng. Chem. Fundam., 1969,**8**,81.

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[6] J. C. R. Reis, J. Chem. Soc. Faraday Trans.,1998,**94**,2385.

[7] J. E. Stutchbury, Aust. J. Chem.,1971,**24**,2431.

[8] S. D. Hamann and F. Smith, Aust. J. Chem.,1971,**24**,2431.

[9] For a detailed report on the properties of liquid mixtures see G. M. Schneider, Pure Appl. Chem.,1983,**55**,479 ; and references therein.

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1.8.1: Enthalpies and Gibbs Energies

By definition, the Gibbs energy,

$$\mathrm{G} = \mathrm{U} + \mathrm{p}\,\mathrm{V} - \mathrm{T}\,\mathrm{S}$$

Enthalpy,

$$\mathrm{H} = \mathrm{U} + \mathrm{p}\,\mathrm{V}$$

Combination of equations (a) and (b) yields an important equation relating Gibbs energy G and enthalpy H.

$$\mathrm{G} = \mathrm{H} - \mathrm{T}\,\mathrm{S}$$

Just as we can never know the thermodynamic energy of a system, so we can never know the enthalpy. Consequently analysis of enthalpies is more complicated than analysis of volumetric properties, bearing in mind that the density of a solution (liquid) can be accurately measured. Differences are therefore emphasised in the context of enthalpies.

A differential change in Gibbs energy at constant temperature is related to the changes in enthalpy dH and entropy, dS.

$$\mathrm{dG} = \mathrm{dH} - \mathrm{T}\,\mathrm{dS}$$

For an isothermal process from state I to state II, the change in Gibbs energy $\Delta\mathrm{G}$ is given by equation (e).

$$\Delta\mathrm{G} = \Delta\mathrm{H} - \mathrm{T}\,\Delta\mathrm{S}$$

Equation (e) signals how enthalpy and entropy changes determine the change in Gibbs energy.

A closed system at temperature T and pressure p is prepared using n_1 moles of solvent (water) and n_j moles of solute-j. The system is at equilibrium such that the composition/organisation is represented by ξ^{eq} and the affinity for spontaneous change is zero. Using an over-defined representation we define the system as follows.

$$\mathrm{G}^{\mathrm{eq}} = \mathrm{G}^{\mathrm{eq}}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \xi^{\mathrm{eq}}, \mathrm{A} = 0\right]$$

Under such circumstances the Gibbs energy G is a minimum G^{eq} when plotted as a function of ξ. The enthalpy of this system can be defined using a similar equation.

$$\mathrm{H}^{\mathrm{eq}} = \mathrm{H}^{\mathrm{eq}}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \xi^{\mathrm{eq}}, \mathrm{A} = 0\right]$$

It is unlikely that H^{eq} corresponds to a minimum in the plot of enthalpy H against ξ. Indeed the same comment applies to the entropy S^{eq};

$$\mathrm{S}^{\mathrm{eq}} = \mathrm{S}^{\mathrm{eq}}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \xi^{\mathrm{eq}}, \mathrm{A} = 0\right]$$

The plots showing the product $\mathrm{T}\,\mathrm{S}$ and H against ξ may not show extrema though taken together they produce a minimum in G at ξ^{eq}.

$$\mathrm{G}^{eq} = \mathrm{H}^{eq} - \mathrm{T}\,\mathrm{S}^{eq}$$

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1.8.2: Enthalpy

There is considerable merit in identifying an extensive property of a closed system called the enthalpy, H. The enthalpy of a closed system is a state variable and defined by equation (a).

$$\mathrm{H} = \mathrm{U} + \mathrm{p}\,\mathrm{V}$$

We identify a given state by the symbol I having enthalpy $\mathrm{H[I]}$, energy $\mathrm{U[I]}$ and volume $\mathrm{V[I]}$ at pressure p.

$$\mathrm{H[I]} = \mathrm{U[I]} + \mathrm{p}\,\mathrm{V[I]}$$

This system is displaced to a neighbouring state such that the differential change in enthalpy is dH. Using equation (a),

$$\mathrm{dH} = \mathrm{dU} + \mathrm{p}\,\mathrm{dV} + \mathrm{V}\,\mathrm{dp}$$

But according to the first law of thermodynamics, the differential change in thermodynamic energy dU is given by '$q - p\,dV$' where q is the heat accompanying the change. Then,

$$\mathrm{dH} = \mathrm{q} - \mathrm{p}\,\mathrm{dV} + \mathrm{p}\,\mathrm{dV} + \mathrm{V}\,\mathrm{dp}$$

or,

$$\mathrm{dH} = \mathrm{q} + \mathrm{V}\,\mathrm{dp}$$

At constant pressure,

$$\mathrm{dH} = \mathrm{q}$$

For a change from state I to state II the change in enthalpy is given by equation (g).

$$\Delta\mathrm{H} = \int_{\mathrm{I}}^{\mathrm{II}} \mathrm{dH} = \mathrm{H(II)} - \mathrm{H(I)} = \mathrm{q}$$

In equation (g) we replace the integral of dH by the difference $\mathrm{H(II)} - \mathrm{H(I)}$ because enthalpy is a state variable and so $\Delta\mathrm{H}$ is independent of the path between the two states and hence so is q. In liquid solutions, the recorded heat is also independent of the rate of change in chemical composition between state I and state II.

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1.8.3: Enthalpy- Thermodynamic Potential

The enthalpy H of a closed system is related by definition to the thermodynamic energy U; $\mathrm{H} = \mathrm{U} + \mathrm{p}\,\mathrm{V}$. But

$$\mathrm{dH} = \mathrm{q} + \mathrm{V}\,\mathrm{dp}$$

From the second law of thermodynamics,

$$\mathrm{T}\,\mathrm{dS} = \mathrm{q} + \mathrm{A}\,\mathrm{d}\xi; \quad \mathrm{A}\,\mathrm{d}\xi \geq 0$$

Then

$$\mathrm{dH} = \mathrm{T}\,\mathrm{dS} + \mathrm{V}\,\mathrm{dp} - \mathrm{A}\,\mathrm{d}\xi; \mathrm{A}\,\mathrm{d}\xi \geq 0$$

Thus all spontaneous processes at constant entropy and pressure (i.e. isentropic and isobaric) lower the enthalpy of a closed system. This conclusion finds application in acoustics where the changes in a system perturbed by a travelling sound wave are discussed in terms of changes in enthalpy at constant entropy and pressure. Confining our attention to systems either at equilibrium (i.e. $\mathrm{A} = 0$) or at fixed ξ, two key relationships follow from equation (c).

$$\mathrm{T} = (\partial \mathrm{H}/\partial \mathrm{S})_{\mathrm{p}}$$

and

$$\mathrm{V} = (\partial \mathrm{H}/\partial \mathrm{p})_{\mathrm{S}}$$

In these terms the extensive variable, volume, is given by the

i. isentropic differential dependence of enthalpy on pressure, and
ii. isothermal differential dependence of Gibbs energy on pressure.

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1.8.4: Enthalpy- Solutions- Partial Molar Enthalpies

The enthalpy of a solution containing n1 moles of water and nj moles of solute, chemical substance j, is defined by the independent variables, T, p, n_1 and n_j.

$$\mathrm{H} = \mathrm{H}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n_j}\right]$$

where [1],

$$\mathrm{H} = \mathrm{n}_1\,\mathrm{H}_1(\mathrm{aq}) + \mathrm{n_j}\,\mathrm{H_j}(\mathrm{aq})$$

Here $\mathrm{H}_1(\mathrm{aq})$ and $\mathrm{H}_j(\mathrm{aq})$ are the partial molar enthalpies of water and solute j in the solution.

$$\mathrm{H}_1(\mathrm{aq}) = \left(\partial \mathrm{H}/\partial \mathrm{n}_1\right)_{\mathrm{T,p,n(j)}}$$

$$\mathrm{H_j}(\mathrm{aq}) = \left(\partial \mathrm{H}/\partial \mathrm{n_j}\right)_{\mathrm{T,p,n(1)}}$$

For a solution prepared using $1\ \mathrm{kg}$ of solvent, water and m_j moles of solute j [2],

$$\mathrm{H}\left(\mathrm{aq}; \mathrm{w}_1 = 1\ \mathrm{kg}\right) = \left(1/\mathrm{M}_1\right)\ \mathrm{H}_1(\mathrm{aq}) + \mathrm{m_j}\,\mathrm{H_j}(\mathrm{aq})$$

The chemical potential of the solvent in an aqueous solution is related to the molality of solute j, m_j using equation (f) where ϕ is the practical osmotic coefficient, a property of the solvent.

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \phi\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}$$

The chemical potential and partial molar enthalpy are linked using the Gibbs-Helmholtz equation such that at fixed pressure, $\mathrm{d}\left(\mu_1(\mathrm{aq})/\mathrm{T}\right)/\mathrm{dT} = -\mathrm{H}_1(\mathrm{aq})/\mathrm{T}^2$. Hence [3]

$$\mathrm{H}_1(\mathrm{aq}) = \mathrm{H}_1^*(\lambda) + \mathrm{R}\,\mathrm{T}^2\,\mathrm{M}_1\,\mathrm{m_j}\left(\mathrm{d}\phi/\mathrm{dT}\right)_\mathrm{p}$$

By definition the practical osmotic coefficient is unity for ideal solutions at all T and p. Then the partial molar enthalpy of the solvent in an ideal solution,

$$\mathrm{H}_1(\mathrm{aq,id}) = \mathrm{H}_1^*(\lambda)$$

The definition of ϕ requires that $\mathrm{limit}\left(\mathrm{m_j} \to 0\right)\mathrm{H}_1(\mathrm{aq})$ equals $\mathrm{H}_1^*(\lambda)$. We express the difference between the partial molar enthalpies of the solvent in real and ideal solutions using a relative (partial) molar enthalpy, $\mathrm{L}_1(\mathrm{aq})$.

$$\mathrm{L}_1(\mathrm{aq}) = \mathrm{H}_1(\mathrm{aq}) - \mathrm{H}_1^*(\lambda)$$

In equation (i), we encounter another difference in order to take account of the fact that we cannot measure absolute enthalpies of solutions and solvents.

The chemical potential of the solute j (at fixed T and p, which is close to ambient pressure) is related to the molality m_j using equation (j).

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)$$

From the Gibbs-Helmholtz Equation,

$$\mathrm{H_j}(\mathrm{aq}) = \mathrm{H_j^0}(\mathrm{aq}) - \mathrm{R}\,\mathrm{T}^2\ \left(\mathrm{d}\ln\gamma_\mathrm{j}/\mathrm{dT}\right)_\mathrm{p}$$

But activity coefficient γ_j is defined such that $\mathrm{limit}\left(\mathrm{m_j} \to 0\right)\gamma_\mathrm{j} = 1.0$ at all T and p. Moreover for an ideal solution, $\gamma_j = 1.0$. Hence,

$$\mathrm{limit}\left(\mathrm{m_j} \to 0\right)\mathrm{H_j}(\mathrm{aq}) = \mathrm{H_j^0}(\mathrm{aq}) = \mathrm{H_j^\infty}(\mathrm{aq})$$

In other words, with increasing dilution $\mathrm{H}_j(\mathrm{aq})$ approaches a limiting partial molar enthalpy $\mathrm{H_j^\infty}(\mathrm{aq})$ which equals the partial molar enthalpy of the solute in an ideal solution. We identify a relative (partial) molar enthalpy of solute j, $\mathrm{L_j}(\mathrm{aq})$.

$$\mathrm{L_j}(\mathrm{aq}) = \mathrm{H_j}(\mathrm{aq}) - \mathrm{H_j^\infty}(\mathrm{aq})$$

Hence, at fixed T and p

$$\text{limit}\,(\mathrm{m_j} \rightarrow 0)\,\mathrm{L_j(aq)} = 0$$

Therefore for simple solutes in solution in the limit of infinite dilution the relative partial molar enthalpy of solute j is zero [4].

Footnotes

[1] $[\mathrm{J}] = [\mathrm{mol}]\ \left[\mathrm{Jmol^{-1}}\right] + [\mathrm{mol}]\ \left[\mathrm{Jmol^{-1}}\right]$

[2] $\left[\mathrm{Jkg^{-1}}\right] = \left[\mathrm{kgmol^{-1}}\right]^{-1}\ \left[\mathrm{Jmol^{-1}}\right] + \left[\mathrm{molkg^{-1}}\right]\ \left[\mathrm{Jmol^{-1}}\right]$

[3] Note the advantage of expressing the composition in terms of molalities rather than in concentrations for which we would have to take account of the dependence of volume on temperature.

[4] An interesting comparison is the molar enthalpy of water(λ) and the limiting molar enthalpy of solute water in a solvent such as methanol. We define a transfer quantity, $\Delta_{\mathrm{tr}}\mathrm{H}^0$ [$= \mathrm{H}^\infty$ ($\mathrm{H_2O}$ as solute in a defined solvent) $-\mathrm{H}_1^*\,(\lambda\mathrm{H_2O})$], characterizing the difference in molar enthalpy of liquid water and the limiting partial molar enthalpy of solute water at ambient pressure and $298.15\ \mathrm{K}$ _. $\Delta_{\mathrm{tr}}\mathrm{H}^0$ is 0.85, 4.05 and $10.11\ \mathrm{kJmol^{-1}}$ in $\mathrm{CH_3OH}(\lambda)$, $\mathrm{C_7H_{15}OH}(\lambda)$ and $\mathrm{C_2H_4(O.CO.C_3H_7)_2}(\lambda)$ respectively [5].

[5] S.-O. Nilsson, J. Chem. Thermodyn., 1986, **18**, 1115.

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1.8.5: Enthalpies- Solutions- Equilibrium and Frozen Partial Molar Enthalpies

A given system at fixed T and p is at thermodynamic equilibrium. The enthalpy of the system is perturbed by adding $\delta \mathrm{n}_j$ moles of chemical substance j. We imagine two possible limiting changes to the system. In one limit the enthalpy of the system changes to a neighbouring state where the extent of chemical reaction remains constant; i.e. at fixed ξ. In another limit the enthalpy of the system changes to a neighbouring state where the affinity for spontaneous change A remains constant. The two differential changes in enthalpy are related.

$$\left(\frac{\partial H}{\partial n_j}\right)_A = \left(\frac{\partial H}{\partial n_j}\right)_\xi - \left(\frac{\partial \mathrm{A}}{\partial n_j}\right)_\xi \left(\frac{\partial \xi}{\partial A}\right)_{n_j} \left(\frac{\partial H}{\partial \xi}\right)_{n_j}$$

We identify the state being perturbed as the equilibrium state where $\mathrm{A} = 0$ and the composition-organisation is represented by \(\xi^{\mathrm{eq}}\). We identify two quantities describing the impact of adding $\delta \mathrm{n}_j$ moles of chemical substance j.

Equilibrium partial molar enthalpy,

$$\mathrm{H_j}(\mathrm{A}=0) = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,A=0}}$$

Frozen partial molar enthalpy,

$$\mathrm{H_j}\left(\xi^{\mathrm{eq}}\right) = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p},\xi^{\mathrm{eq}}}$$

Because the triple product term on the r.h.s. of equation (a) is not zero at equilibrium (i.e. at $\mathrm{A} =$ zero and $\xi = \xi^{\mathrm{eq}}$), then $\mathrm{H_j}(\mathrm{A}=0)$ is not equal to. By convention, the term ‘ partial molar enthalpy is taken to mean $\mathrm{H_j}(\mathrm{A}=0)$.

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1.8.6: Enthalpies- Neutral Solutes

A given aqueous solution at temperature T and pressure p (close to ambient pressure p^0) is prepared using n_1 moles of water and n_j moles of a solute, chemical substance-j. The enthalpy of this solution $\mathrm{H(aq)}$ is given by equation (a) where $\mathrm{H}_1\mathrm{(aq)}$ and $\mathrm{H}_j\mathrm{(aq)}$ are the (equilibrium) partial molar enthalpies of solvent and solute respectively

$$\mathrm{H(aq) = n_1\,H_1(aq) + n_j\,H_j(aq)}$$

$$\mathrm{H_1(aq) = \left(\frac{\partial H}{\partial n_1}\right)_{T,p,n(j)}}$$

$$\mathrm{H_j(aq) = \left(\frac{\partial H}{\partial n_j}\right)_{T,p,n(1)}}$$

Then [1,2],

$$\mathrm{H_1(aq) = H_1^*(\lambda) + R\,T^2\,M_1\,m_j\left(\frac{\partial \phi}{\partial T}\right)_p}$$

$$\mathrm{limit\,(m_j \rightarrow 0)\,H_1(aq) = H_1^*(\lambda)}$$

Similarly for the solute, chemical substance j (assuming ambient pressure p is close to the standard pressure) [3,4],

$$\mathrm{H_j(aq) = H_j^{\infty}(aq) - R\,T^2\left(\frac{\partial \ln(\gamma_j)}{\partial T}\right)_p}$$

$\mathrm{H_j^{\infty}(aq)}$ is the limiting (infinite dilution) partial molar enthalpy of solute j. The enthalpy of a solution prepared using n_1 moles of water and n_j moles of solute is given by equation (g).

$$\mathrm{H(aq) = n_1\,\left[H_1^*(\lambda) + R\,T^2\,M_1\,m_j\,(\partial\phi/\partial T)_p\right]} \\ \mathrm{+n_j\,\mid H_j^{\infty}(aq) - R\,T^2\,(\partial \ln \gamma_j/\partial T)_p\big]}$$

For a solution in $1\ \mathrm{kg}$ of water,

$$\mathrm{H\,(aq; w_1 = 1\ kg) = (1/M_1)\,\left[H_1^*(\lambda) + R\,T^2\,M_1\,m_j\,(\partial\phi/\partial T)_p\right]} \\ \mathrm{+\,m_j\,\left[H_j^{\infty}(aq) - R\,T^2\,(\partial \ln \gamma_j/\partial T)_p\right]}$$

We re-arrange equation (h).

$$\mathrm{H\,(aq; w_1 = 1\ kg) = (1/M_1)\,H_1^*(\lambda)} \\ \mathrm{+\,m_j\,\left[H_j^{\infty}(aq) + R\,T^2\,(\partial\phi/\partial T)_p - R\,T^2\,(\partial \ln \gamma_j/\partial T)_p\right]}$$

Equation (i) is interesting because inside the brackets [….] we have the limiting partial molar enthalpy of the solute and two terms which describe the extent to which the enthalpic properties of the solution differ from those of the corresponding ideal solution. We find it advantageous to describe the property in the brackets […] as the apparent molar enthalpy of the solution, $\phi\,(\mathrm{H_j})$. By definition,

$$\mathrm{\phi\,(H_j) = H_j^{\infty}(aq) - R\,T^2\,(d \ln \gamma_j/dT)_p + R\,T^2\,(d\phi/dT)_p}$$

For a solution prepared using $1\ \mathrm{kg}$ of solvent water.

$$\mathrm{H\,(aq; w_1 = 1\ kg) = (1/M_1)\,H_1^*(\lambda) + m_j\,\phi\,(H_j)}$$

But at all T and p,

$$\mathrm{limit\,(m_j \rightarrow 0)\,\gamma_j = 1.0; \ln(\gamma_j) = 0; \phi = 1.0}$$

Hence,

$$\mathrm{limit\,(m_j \rightarrow 0)\,[\partial \ln(\gamma_j)/\partial T]_p = [\partial\phi/\partial T]_p = 0}$$

$$\mathrm{limit\,(m_j \rightarrow 0)\,\phi\,(H_j) = \phi\,(H_j)^{\infty} = H_j^{\infty}(aq)}$$

We recognize a crucial complication in the treatment of the enthalpies of solutions. Unlike volumetric properties of solutions, we cannot measure the enthalpy of a solution. In other words we need to examine differences. Based on equation (k) we form an equation for the enthalpy of the corresponding solution having thermodynamic properties which are ideal.

$$\mathrm{H\,(aq;\,w_1 = 1\ kg;\,id)} = (1/\mathrm{M_1})\ \mathrm{H_1^*}(\lambda) + \mathrm{m_j}\,\phi\,(\mathrm{H_j})^{\infty}$$

The difference between the two enthalpies is given by equation (p)

$$\mathrm{H\,(aq;\,w_1 = 1\ kg)} - \mathrm{H\,(aq;\,w_1 = 1\ kg;\,id)} = \mathrm{m_j}\ [\phi\,(\mathrm{H_j}) - \phi\,(\mathrm{H_j})^{\infty}]$$

Interesting descriptions of the enthalpies of solutions containing simple solutes are based on the concept of excess thermodynamic properties and pairwise solute-solute interaction parameters. Equation (k) describes the enthalpy of a solution prepared using $1\ \mathrm{kg}$ of water whereas equation (o) describes the enthalpy of the corresponding solution where the thermodynamic properties are ideal. The excess enthalpy $\mathrm{H^E\,(aq;\,m_j)}$ is given by equation (q).

$$\mathrm{H^E\,(aq;\,m_j)} = \mathrm{h_{ij}}\ \left(\mathrm{m_j/m^0}\right)^2 + \mathrm{h_{iji}}\ \left(\mathrm{m_j/m^0}\right)^3 \ldots\ldots$$

Footnotes

[1] For the solvent in solutions (at constant pressure),

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \phi\,\mathrm{R\,T\,M_1\,m_j}$$

But

$$-\frac{\mathrm{H_1(aq)}}{\mathrm{T^2}} = \frac{\partial\,[\mu_1(\mathrm{aq})/\mathrm{T}]}{\partial T}$$

Then $-\frac{\mathrm{H_1(aq)}}{\mathrm{T^2}} = -\frac{\mathrm{H_1^*}(\lambda)}{\mathrm{T^2}} - \mathrm{R\,M_1\,m_j}\left(\frac{\partial\phi}{\partial \mathrm{T}}\right)_{\mathrm{p}}$

[2] $\mathrm{R\,T^2}\left(\frac{\partial\phi}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \left[\mathrm{JK^{-1}\ mol^{-1}}\right]\ [\mathrm{K}]^2\,[\mathrm{K}]^{-1} = \left[\mathrm{Jmol^{-1}}\right]$

[3] From $\mu_j(\mathrm{aq}) = \mu_{\mathrm{j}}^0(\mathrm{aq}) + \mathrm{R\,T}\ \ln\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m^0}\right)$ Then, $-\frac{\mathrm{H_j(aq)}}{\mathrm{T^2}} = -\frac{\mathrm{H_j^{\infty}(aq)}}{\mathrm{T^2}} + \mathrm{R}\left(\frac{\partial \ln(\gamma_{\mathrm{j}})}{\partial \mathrm{T}}\right)_{\mathrm{p}}$

[4] $\mathrm{R\,T^2}\left(\frac{\partial \ln(\gamma_{\mathrm{j}})}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \left[\mathrm{JK^{-1}\ mol^{-1}}\right]\ [\mathrm{K}]^2\,[\mathrm{K}]^{-1} = \left[\mathrm{Jmol^{-1}}\right]$

[5] See for example,

a. amides(aq) and peptides(aq); A. H. Sijpkes, A. A. C. Oudhuis, G. Somsen and T. H. Lilley, J. Chem. Thermodyn.,1989,**21**,343.
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1.8.7: Enthalpies- Solutions- Dilution- Simple Solutes

A given (old) aqueous solution is prepared using n_1(old) moles of water(λ) and n_j moles of a simple neutral solute at fixed T and p. The enthalpy $H(aq; old)$ of this solution is expressed in terms of the molar enthalpy of water(λ), $H_1^*(\lambda)$ and the apparent molar enthalpy of the solute $\phi\,(H_j;\ old\ )$.

$$H(aq;\ old\ ) = n_1(\ old\ )\,H_1^*(\lambda) + n_j\,\phi\,(H_j;\ old\ )$$

We use the description 'old' because we envisage preparing a 'new' solution by adding n_1(added) moles of water, enthalpy $n_1(\ added\ )\,H_1^*(\lambda)$.

$$H(\ added\ ) = n_1(\ added\ )\,H_1^*(\lambda)$$

The enthalpy of the resultant solution is $H(aq;\ new\ )$;

$$H(\ aq;\ new\ ) = [n_1(old) + n_1(\ added\ )]\ H_1^*(\lambda) + n_j\,\phi\,(H_j;\ new\ )$$

In effect the 'old' solution has been diluted.

$$\Delta H(\ old\ \rightarrow\ new\ ) = H(aq;\ new\ ) - H(\ aq\ ;\ old\ ) - [n_1\ (added\ )\ H_1^*(\lambda)]$$

Hence,

$$\Delta H(\ old\ \rightarrow\ new\ ) = n_j\ [\phi\,(H_j\ (new\ ) - \phi\,(H_j\ (old\ )]$$

An isobaric calorimeter measures heat q characterising the dilution.

$$\begin{aligned} q/n_j &= \Delta_{dil}H\,[m_j(old) \rightarrow m_j(\ new\ )] \\ &= \Delta H(\ old\ \rightarrow\ new\ )/n_j = \phi\,(H_j(j;\ new\ )) - \phi\,(H_j(j; old)) \end{aligned}$$

We imagine a series of experiments in which the molality of solute at the start of the experiment is m_j(I). Following dilution the molality is m_j(II).

$$\Delta_{dil}H\,[m_j(I) \rightarrow m_j(II)] = \phi\,(H_j; m_j; II) - \phi\,(H_j; m_j; I)$$

In a calorimetric experiment we record heat q accompanying a second dilution. Hence,

$$\Delta_{dll}H\,[m_j(II) \rightarrow m_j(III)] = \phi\,(H_j; m_j;\ III\ ) - \phi\,(H_j; m_j;\ II\ )$$

In a third dilution we have that

$$\Delta_{dil}H\,[m_j(III) \rightarrow m_j(IV)] = \phi\,(H_j; m_j; IV) - \phi\,(H_j; m_j;\ III\ )$$

In this experiment the molality of the solution in the sample cell is gradually falling. Combination of the results described by equations (g), (h) and (i) yields the set, $\Delta_{dil}H\,[m_j(I) \rightarrow m_j(II)]\,, \Delta_{dil}H\,[m_j\ (II)\ \rightarrow m_j(III)]\,, \Delta_{dil}H\,[m_j(III) \rightarrow m_j(IV)]\,...$ This set is expanded with further dilutions until by extrapolation we obtain for solution $\Delta_{dil}\,H\,[m_j(I) \rightarrow\ infinite\ dilution\ ]$. We obtain the enthalpies of dilution for all dilutions in a given set of experiments; i.e. for dilution for solutions II, III, IV…

Alternatively a given solution is diluted by increasing amounts of solvent; e.g. adding ethanol(λ) to a solution of urea in ethanol [1].

In the analysis of enthalpies of solutions simplification of the algebra is achieved by defining a number of L-variables, signalling differences in enthalpies. The relative enthalpy L describes the difference between the enthalpies of real and ideal solutions. For a solution prepared using $w_1\ kg$ of solvent (e.g. water),

$$L\,(aq; w_1\ kg) = H\,(aq; w_1\ kg) - H\,(aq; w_1\ kg; id)$$

By definition for the solvent,

$$L_1(aq) = H_1(aq) - H_1^*(\lambda)$$

For the solute j,

$$L_j(aq) = H_j(aq) - H_j^{\infty}(aq)$$

$L_1(aq)$ and $L_j(aq)$ are the relative partial molar enthalpies of solvent and solute respectively. Similarly in terms of apparent properties,

$$\phi\left(L_j\right)=\phi\left(H_j\right)-\phi\left(H_j\right)^{\infty}$$

$$L=n_1 L_1+n_j L_j=n_j \phi\left(L_j\right)$$

$\phi(L_j)$ is the apparent relative molar enthalpy of solute j in solution at molality m_j, describing the difference between the apparent molar enthalpies of solute j in real and ideal solutions. In other words we have a direct probe of the role of solute-solute interactions in solution. Both L and $\phi(L_j)$ are (by definition) zero for solutions where the thermodynamic properties are ideal.

This galaxy of variables is clarified if we return to a calorimetric experiment where a solution is diluted. An (old) aqueous solution is prepared using n_1 moles of water(λ) and n_j moles of solute producing a solution having enthalpy $H(aq;old)$.

$$H(aq;\ old\ )=n_1(\ old\ ) H_1^*(\lambda)+n_j \phi\left(H_j;\ old\ \right)$$

To this solution we add (at the same T and p) n_1(added) moles of water(λ).

$$H(\ added\ )=n_1(\ added\ ) H_1^*(\lambda)$$

in the limit that n_1(added) is sufficiently large that the molality m_j of the 'new' solution is negligibly small, then

$$\text{limit}\left(\ new\ ; m_j \rightarrow 0\right) \phi\left(H_j;\ new\ \right)=\phi\left(H_j\right)^{\infty}$$

$$\Delta H(\ old\ \rightarrow\ new\ )=-n_j \phi\left(L_j\right)$$

By definition,

$$\Delta_{dil} H=\Delta H(\ old\ \rightarrow\ new\ ) / n_j$$

$$\Delta_{dil} H=-\phi\left(L_j\right)$$

Consistent with our definitions of heat q and enthalpy change, a positive $\Delta_{dil}H$ indicates that dilution is endothermic.

We have not commented on the dependence of either $\phi\left(L_j\right)$ or $\phi\left(H_j\right)$ on molality of solute. In order to say something about these variables we need explicit equations for these dependences on composition of solution.

An important approach to the description of the properties of solutions uses excess thermodynamic functions. The quantity $L(aq)$ defined in equation (n) refers to a solutions prepared using n_1 moles of solvent and n_j moles of solute, contrasting the properties of real and ideal solutions. The excess enthalpy H^E refers to the corresponding solutions prepared using $1\ kg$ of water and m_j moles of solute j.

$$H^E=H\left(aq; w_1=1\ kg; m_j\right)-H\left(aq; w_1=1\ kg; m_j; id\right)$$

thus,

$$H^E=\left[(1/M_1)\ H_1^*(\lambda)+m_j \phi\left(H_j\right)\right]-\left[(1/M_1)\ H_1^*(\lambda)+m_j \phi\left(H_j\right)^{\infty}\right]$$

Or,

$$H^E=m_j\ \left[\phi\left(H_j\right)-\phi\left(H_j\right)^{\infty}\right]$$

Therefore

$$H^E=m_j \phi\left(L_j\right)$$

Again the development of equation (x) reflects our continuing interest in **differences** with respect to enthalpies. Nevertheless the key isobaric calorimetric equation requires that the measured ratio ($q/\ n_j$) for the process solvent + solute forming an ideal solution (at fixed T and p) equals the standard enthalpy of solution for pure substance j, $\Delta_{sln}H^0$. For neutral solutes, the dependence of

partial molar enthalpy of solute $H_j(aq)$ on solute molality mj is small such that the recorded $(q/\ n_j)$ for real solutions can often be equated to the corresponding limiting enthalpy of solution, $\Delta_{s\,ln}H^0$ because in an ideal solution the standard partial molar enthalpy of a solute equals the partial molar enthalpy of the solute at infinite dilution. For solute j,

$$\Delta_{s\,ln}H_j^0 = \Delta_{s\,ln}H_j^\infty = H_j^\infty(aq) - H_j^*(\ s)$$

Significantly modern calorimeters are sufficiently sensitive to measure heat q when a known but small amount of substance j is dissolved in a known amount of solvent. In many cases the dependence of $\Delta_{sin}H$ ion solute molality is, for small neutral solutes, negligibly small such that $\Delta_{sin}H$ is assumed to equal $\Delta_{sin}H^0$ [2].

Heats of solution can be analysed in terms of group contributions to the enthalpy of solution for a given series of solutes [3]. Moreover the dependence of $\Delta_{sin}H^\infty$ for a given solute on temperature yields the corresponding limiting isobaric heat capacity of solution, $\Delta_{s\,ln}C_p^\infty$ [4]. In fact by measuring $\Delta_{sin}H^\infty$ for solutes in two solvents, the derived property is the standard enthalpy of transfer [5].

$$\begin{aligned}\Delta_{s\,ln}H_j^\infty &\text{ solvent B} \rightarrow \text{ solvent A)} \\ &= \Delta_{s\,ln}H_j^\infty(\text{ solvent A}) - \Delta_{s\,ln}H_j^\infty(\text{ solvent B})\end{aligned}$$

Such a study identified a quite striking extremum for limiting partial molar enthalpies of solution for $NaBH_4$ in water + 2-methylpropan-2-ol mixtures at low alcohol mole fractions and $298.2\ K$ and hence a quite striking reversal of sign in limiting partial molar isobaric heat capacities for $NaBPh_4$ in this binary aqueous mixture [5]; see also data for dialkyl sulfonates in alcohol + water mixtures [6] and tri-n-alkyl phosphates in water + DMF binary mixtures [7]. Indeed an extensive literature describes the enthalpies of solution for neutral solutes and, where the results concern one solute in two or more solvents, the corresponding enthalpy of transfer; cf. equation (z) [8].

Where the results describe a series of closely related neutral solutes, it is often possible to estimate contributions from individual groups (e.g. CH_2 and OH) to a given limiting enthalpy of transfer [9].

In many reports, the results of calorimetric experiments show clear evidence of a dependence of partial molar enthalpy of a given solute on molality of the solution. One of the first reports of such a dependence for neutral solutes was published in 1940 [10]. Hence a direct signal is obtained of enthalpic solute-solute interactions in solution.

An aqueous solution is prepared using water($w_1 = 1\ kg$) and m_j moles of solute j at defined T and p.

$$H\,(aq; w_1 = 1\ kg) = (1/M_1)\ H_1(aq) + m_j\,H_j(aq)$$

In the event that the thermodynamic properties of this solutions are ideal the enthalpy of the solution is given by equation (zb).

$$H\,(aq; w_1 = 1\ kg; id) = (1/M_1)\ H_1^*(\lambda) + m_j\,H_j^\infty(aq)$$

The excess enthalpy $H^E\,(aq; m_j)$ is given by equation (zc).

$$H^E\,(aq; m_j) = H\,(aq; w_1 = 1\ kg) - (1/M_1)\ H_1^*(\lambda) - m_j\,H_j^\infty(aq)$$

$H^E\,(aq; m_j)$ can be expressed as a power series in molality m_j.

$$H^E\,(aq; m_j) = h_{jj}\ \left(m_j/m^0\right)^2 + h_{ij}\ \left(m_j/m^0\right)^3$$

A given solution contains solute j such that an isobaric calorimeter is used to measure the heat of dilution. We obtain the enthalpy per mole of solute on going from molality m_j(initial) to m_j(final), $\Delta_{dil}H$.

$$\Delta_{dil}H = H^E\,(m_j\text{ - final }) / m_j(\text{ final }) - H^E\,(m_j - \text{ initial }) / m_j\ (\text{initial})$$

Equations (zd) and (ze) yield an equation for measured $\Delta_{dil}H$ in terms of enthalpic solute-solute pairwise and triplet interaction parameters.

$$\begin{aligned}\Delta_{dil}H = h_{ij}\ &[m_j(\text{ final }) - m_j(\text{ initial })]\ /m^0 \\ &+ h_{jij}\ \left[\{m_j(\text{ final })\}^2 - \{m_j(\text{ initial })\}^2\right] / \left(m^0\right)^2\end{aligned}$$

In most cases, authors concentrate attention on pairwise interaction parameters [11] between identical (homotactic) and different (heterotactic) solute molecules in a given solution [12]. The concept of solute-solute pairwise (and higher order) interaction parameters allows quite detailed patterns to emerge from enthalpies of dilution of neutral solutes in salt solution [13].

Footnotes

[1] E.g. adding ethanol(λ) to a solution of urea in ethanol(λ) ; D. Hamilton and R. H. Stokes, J. Solution Chem.,1972,**1**,223.

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1.8.8: Enthalpies- Solutions- Simple Solutes- Interaction Parameters

The excess Gibbs energy $\mathrm{G^E}$ for a dilute aqueous solution containing a simple solute j prepared using $1\ \mathrm{kg}$ of solvent, water is given by equation (a).

$$\mathrm{G^E = R\,T\,m_j\ [1 - \phi + \ln(\gamma_j)]}$$

In terms of Gibbs energies pairwise solute-solute interaction parameters,

$$\mathrm{G^E = g_{jj}\ \left[m_j/m^0\right]^2}$$

The excess enthalpy[1]

$$\mathrm{H^E = h_{ij}\ \left[m_j/m^0\right]^2}$$

where [cf. Gibbs –Helmholtz Equation],

$$\mathrm{h_{ij} = -T^2\ \{\partial\left[g_{jj}/T\right]/\partial T\}_p}$$

Here $\mathrm{h_{jj}}$ is the pairwise solute-solute enthalpic interaction parameter. For the solvent,

$$\mu_1(\mathrm{aq}) = \mu_1^*(\lambda) - \mathrm{R\,T\,M_1\,m_j - M_1\,g_j\ \left(m_j/m^0\right)^2}$$

Using the Gibbs-Helmholtz Equation,

$$\mathrm{H_1(aq) = H_1^*(\lambda) - M_1\,h_{ij}\ \left(m_j/m^0\right)^2}$$

For the solute,

$$\mu_j(\mathrm{aq}) = \mu_j^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_j/m^0\right) + 2\,g_{ij}\ \left(m^0\right)^{-2}\ m_j}$$

Then using the Gibbs-Helmholtz Equation [2]

$$\mathrm{H_j(aq) = H_j^\infty(aq) + 2\,h_{ij}\ \left(m^0\right)^{-2}\ m_j}$$

Alternatively we may express the enthalpy of the solution in terms of the apparent molar enthalpy of the solute, $\phi\,(\mathrm{H_j})$.

$$\mathrm{H\,(aq;\,w_1 = 1\ kg) = (1/M_1)\ H_1^*(\lambda) + m_j\,\phi\,(H_j)}$$

For the ideal solution,

$$\mathrm{H\,(aq;\,id;\,w_1 = 1\ kg) = (1/M_1)\ H_1^*(\lambda) + m_j\,\phi\,(H_j)^\infty}$$

where $\phi\,(\mathrm{H_j})^\infty = \mathrm{H_j^\infty(aq)}$. Then

$$\mathrm{H^E = m_j\ [\phi\,(H_j) - \phi\,(H_j)^\infty]}$$

Hence using equation (c),

$$\mathrm{\phi\,(H_j) = \phi\,(H_j)^\infty + h_{ji}\ \left(m^0\right)^{-2}\ m_j}$$

We use these equations in the analysis of a calorimetric data where a given solution is diluted. The solution is prepared using $\mathrm{n_1}$ moles of solvent (water) and n_j moles of a simple solute j. Then

$$\mathrm{H(I;\,aq) = n_1\,H_1^*(\lambda) + n_j\,\phi\,(H_j;\,I;\,aq)}$$

A new solution is prepared by adding (in the calorimeter) $\Delta\mathrm{n_1}$ moles of solvent, Then

$$\mathrm{H(II;\,aq) = (n_1 + \Delta n_1)\ H_1^*(\lambda) + n_j\,\phi\,(H_j;\,II;\,aq)}$$

Thus the molality of solute j changes from m_j(I) $[= \mathrm{n_j/n_1\,M_1}]$ to m_j(II) $[= \mathrm{n_j/\,(n_1 + \Delta n_1)\ M_1}]$. Therefore,

$$\mathrm{\phi\,(H_j;\,I;\,aq) = \phi\,(H_j)^\infty + \left[h_{ij}\ \left(m^0\right)^{-2}\ n_j/n_1\,M_1\right]}$$

And

$$\phi\left(\mathrm{H_j;II;aq}\right) = \phi\left(\mathrm{H_j}\right)^{\infty} + \left[\mathrm{h_j}\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{n_j}/\left(\mathrm{n_1} + \Delta\mathrm{n_1}\right)\ \mathrm{M_1}\right]$$

In fact we record the heat q (at constant pressure) when $\Delta\mathrm{n_1}$ moles of solvent are added to solution I to form solution II. Thus,

$$\mathrm{q} = \mathrm{H(II;aq)} - \mathrm{H(I;aq)} - \Delta\mathrm{n}\,\mathrm{H_1^*}(\lambda)$$

Footnotes

[1] From equation (a) and (b) $\mathrm{G^E} = \left[\mathrm{Jkg^{-1}}\right]$ From equation (c) $\mathrm{H^E} = \left[\mathrm{Jkg^{-1}}\right]$

[2] A check on the equations with reference to solution prepared using $1\ \mathrm{kg}$ of solvent.

$$\mathrm{H\left(aq;w_1 = 1\ kg\right)} = \left(1/\mathrm{M_1}\right)\ \left[\mathrm{H_1^*}(\lambda) - \mathrm{M_1\,h_{ji}}\ \left(\mathrm{m_j/m^0}\right)^2\right] + \mathrm{m_j}\ \left[\mathrm{H_j^{\infty}(aq)} + 2\,\mathrm{h_{jj}}\ \left(\mathrm{m}^0\right)^{-2}\ \mathrm{m_j}\right]$$

Or,

$$\mathrm{H\left(aq;w_1 = 1\ kg\right)} = \left(1/\mathrm{M_1}\right)\ \mathrm{H_1^*}(\lambda) - \mathrm{h_{jj}}\ \left(\mathrm{m_j/m^0}\right)^2 + \mathrm{m_j\,H_j^{\infty}(aq)} + 2\,\mathrm{h_{ij}}\ \left(\mathrm{m_j/m^0}\right)^2$$

Then

$$\mathrm{H\left(aq;w_1 = 1\ kg\right)} = \left(1/\mathrm{M_1}\right)\ \mathrm{H_1^*}(\lambda) + \mathrm{m_i\,H_i^{\infty}(aq)} + \mathrm{H^E}$$

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1.8.9: Enthalpies- Salt Solutions- Apparent Molar- Partial Molar and Relative Enthalpies

Description of the enthalpies of salt solutions is similar to that given for neutral solutes except that account is taken of the fact that one mole of a given salt can with complete dissociation produce v moles of ions. The chemical potential of the solvent in an aqueous salt solution (at constant temperature and ambient pressure) is given by equation (a).

$$\mu_1(\mathrm{aq}) = \mu_1^{\star}(\lambda) - \mathrm{v}\,\phi\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}$$

Here ϕ is the practical osmotic coefficient where $\mathrm{limit}\,(\mathrm{m_j} \rightarrow 0)\,\phi = 1.0$ at all T and p. Using the Gibbs-Helmholtz Equation,

$$\mathrm{H}_1(\mathrm{aq}) = \mathrm{H}_1^{*}(\lambda) + \mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,\mathrm{M}_1\,\mathrm{m_j}\,(\partial\phi/\partial\mathrm{T})_{\mathrm{p}}$$

Also

$$\mathrm{limit}\,(\mathrm{m_j} \rightarrow 0)\,\mathrm{H}_1(\mathrm{aq}) = \mathrm{H}_1^{*}(\lambda)$$

By definition,

$$\mathrm{L}_1(\mathrm{aq}) = \mathrm{H}_1(\mathrm{aq}) - \mathrm{H}_1^{*}(\lambda)$$

The chemical potential of a salt j in aqueous solution is given by equation (e).

$$\mu_j(aq) = \mu_j^0(aq) + v\,RT\,\ln\left(Q\,m_j\,\gamma_{\pm}/m^0\right)$$

where, at all T and p,

$$\mathrm{limit}\,(\mathrm{m_j} \rightarrow 0)\,\gamma_{\pm} = 1.0$$

Using the Gibbs-Helmholtz Equation,

$$\mathrm{H_j}(\mathrm{aq}) = \mathrm{H_j^0}(\mathrm{aq}) - \mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,\left[\partial\ln\left(\gamma_{\pm}\right)/\partial\mathrm{T}\right]_{\mathrm{p}}$$

For a salt solution having ideal thermodynamic properties,

$$\mathrm{H_j}(\mathrm{aq;id}) = \mathrm{H_j^0}(\mathrm{aq}) = \mathrm{H_j^{\infty}}(\mathrm{aq})$$

By definition, the relative partial molar enthalpy of the salt,

$$\mathrm{L_j}(\mathrm{aq}) = \mathrm{H_j}(\mathrm{aq}) - \mathrm{H_j^{\infty}}(\mathrm{aq})$$

In the limit of infinite dilution the relative partial molar enthalpy of a salt is zero. Thus

$$\mathrm{limit}\,(\mathrm{m_j} \rightarrow 0)\,\mathrm{L_j}(\mathrm{aq}) = 0$$

For a solution prepared using $\mathrm{w}_1\ \mathrm{kg}$ of water(λ),

$$\begin{aligned}\mathrm{H}\,(\mathrm{aq};\mathrm{w}_1\ \mathrm{kg}) = {} & \mathrm{n}_1\,\mathrm{H}_1^{*}(\lambda) + \mathrm{n}_1\,\mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,\mathrm{M}_1\,\mathrm{m_j}\,(\partial\phi/\partial\mathrm{T})_{\mathrm{p}} \\ & + \mathrm{n_j}\,\mathrm{H_j^0}(\mathrm{aq}) - \mathrm{n_j}\,\mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,\left[\partial\ln\left(\gamma_{\pm}\right)/\partial\mathrm{T}\right]_{\mathrm{p}}\end{aligned}$$

But

$$\mathrm{n}_1\,\mathrm{m_j} = \mathrm{n}_1\,\mathrm{n_j}/\mathrm{w}_1 = \mathrm{n_j}/\mathrm{M}_1$$

$$\begin{aligned}\mathrm{H}\,(\mathrm{aq};\mathrm{w}_1\ \mathrm{kg}) = {} & \mathrm{n}_1\,\mathrm{H}_1^{*}(\lambda) + \mathrm{n_j}\,\mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,(\partial\phi/\partial\mathrm{T})_{\mathrm{p}} \\ & + \mathrm{n_j}\,\mathrm{H_j^0}(\mathrm{aq}) - \mathrm{n_j}\,\mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,\left[\partial\ln\left(\gamma_{\pm}\right)/\partial\mathrm{T}\right]_{\mathrm{p}}\end{aligned}$$

$$\begin{aligned}\mathrm{H}\,(\mathrm{aq};\mathrm{w}_1\ \mathrm{kg}) = {} & \mathrm{n}_1\,\mathrm{H}_1^{*}(\lambda) + \mathrm{n_j}\,\left\{\mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,(\partial\phi/\partial\mathrm{T})_{\mathrm{p}}\right. \\ & \left. + \mathrm{H_j^{\infty}}(\mathrm{aq}) - \mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,\left[\partial\ln\left(\gamma_{\pm}\right)/\partial\mathrm{T}\right]_{\mathrm{p}}\right\}\end{aligned}$$

The term in the brackets {….} defines the apparent molar enthalpy of salt j, $\phi\,(\mathrm{H_j})$.

$$\phi\,(\mathrm{H_j}) = \mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,(\partial\phi/\partial\mathrm{T})_{\mathrm{p}} + \mathrm{H_j^{\infty}}(\mathrm{aq}) - \mathrm{v}\,\mathrm{R}\,\mathrm{T}^2\,\left[\partial\ln\left(\gamma_{\pm}\right)/\partial\mathrm{T}\right]_{\mathrm{p}}$$

Using equation (o),

$$\mathrm{H\,(aq;w_1\ kg)} = \mathrm{n_1\,H_1^*}(\lambda) + \mathrm{n_j}\,\phi\,(\mathrm{H_j})$$

In other words we have grouped all the parameters describing the properties of the salt in a real solution under a single term, $\phi(\mathrm{H}_j)$. For a solution prepared using $1\ \mathrm{kg}$ of water,

$$\mathrm{H\,(aq;w_1 = 1\ kg)} = (1/\mathrm{M_1})\ \mathrm{H_1^*}(\lambda) + \mathrm{m_j}\,\phi\,(\mathrm{H_j})$$

At all T and p,

$$\mathrm{limit\ (m_j \to 0)}\ \gamma_\pm = 1; \ln(\gamma_\pm) = 0; \phi = 1$$

Hence,

$$\mathrm{limit\ (m_j \to 0)}\ [\partial \ln(\gamma_\pm)/\partial \mathrm{T}]_\mathrm{p} = [\partial\phi/\partial \mathrm{T}]_\mathrm{p} = 0$$

$$\mathrm{limit\ (m_j \to 0)}\ \phi\,(\mathrm{H_j}) = \mathrm{H_j^\infty(aq)}$$

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1.8.10: Enthalpy of Solutions- Salts

The chemical substance $\mathrm{NaCl(s)}$ is a hard crystalline solid with a high melting point, $1074\mathrm{K}$. All the more remarkable therefore is the observation when a few crystals are dropped into water(ℓ) the crystals disintegrate into ions with no dramatic change in the temperature of the water. One concludes that the intensity of interactions between ions in the crystal is comparable to that between ions and water molecules in the aqueous solution. Not surprisingly therefore enthalpies of solutions have been extensively investigated.

The enthalpy of an aqueous solution prepared at temperature T and pressure p using $\mathrm{n_1}$ moles of water and n_j moles of salt is given by equation (a) where $\phi\,(\mathrm{H}_j)$ is the apparent molar enthalpy of salt j in solution.

$$\mathrm{H(aq) = n_1\,H_1^*(\ell) + n_j\,\phi\,(H_j)}$$

Before the solution was prepared the enthalpy of the system, $\mathrm{H(no-mix)}$ is given by equation (b) where $\mathrm{H_j^*(\,s)}$ is the molar enthalpy of solid salt j.

$$\mathrm{H(no-mix) = n_1\,H_1^*(\ell) + n_j\,H_j^*(\,s)}$$

Using an isobaric calorimeter, heat q is recorded for the solution process.

$$\mathrm{q = H(aq) - H(no-mix) = n_j\,\left[\phi\,(H_j) - H_j^*(\,s)\right]}$$

Or

$$\phi\,(H_j) - H_j^*(s) = q/n_j$$

In many studies [1] using sensitive calorimeters ($\mathrm{q/n}_j$) can be recorded for the production of quite dilute solutions such that $\phi\,(\mathrm{H}_j)$ is effectively equal to $\mathrm{H_j^\infty(aq)}$. In other cases $\Delta_{s\,ln}\mathrm{H(s \rightarrow aq)}$ is found to depend on the molality of the resultant solution. One procedure [2] fits the measured enthalpy of solution to a quadratic in the molality of salt.

$$\mathrm{\Delta_{s\,ln}H(s \rightarrow aq) = \Delta_{sln}H^0(\,s \rightarrow aq) + A\,\left(m_j/m^0\right) + B\,\left(m_j/m^0\right)^2}$$

In other cases the Debye-Huckel limiting law is used as a basis for extrapolating $\Delta_{s\,ln}\mathrm{H(s \rightarrow aq)}$ to the required infinite dilution value [3].

Footnotes

[1]

a. R. K. Mohanty, T. S. Sarma, S. Subramanian and J.C. Ahluwalia, Trans. Faraday Soc.,1971,**67**,305.
b. N Van Meurs, Th. W Warmerdam and G. Somsen, Fluid Phase Equilib., 1989,**49**,263.
c. M. E. Estep, D. D. Macdonald and J. B. Hyne, J. Solution Chem.,1977,**6**,129.

[2] C. V. Krishnan and H. L. Friedman, J. Phys.Chem.,1970,**74**,3900 .

[3] e.g. Om. N. Bhatnagar and C. M. Criss, J. Phys Chem.,1969,**73**,174.

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1.8.11: Enthalpies- Salt Solutions- Dilution

One mole of salt in solution can, with complete dissociation, produce ν moles of ions. Hence for a given solution prepared using $\mathrm{n_1}$ moles of water(ℓ) and n_j moles of salt, the enthalpy $\mathrm{H\,(aq;w_1\ kg)}$ is given by equation (a).

$$\begin{aligned}&\mathrm{H\,(aq;w_1\ kg)} = \\ &\mathrm{n_1}\left[\mathrm{H_1^*}(\ell) + \mathrm{v\,R\,T^2\,m_j}\,(\partial\phi/\partial\mathrm{T})_\mathrm{p}\right] \\ &\quad + \mathrm{n_j}\left[\mathrm{H_j^\infty}(\mathrm{aq}) - \mathrm{v\,R\,T^2\,M_1\,m_j}\,(\partial \ln\gamma_\pm/\partial\mathrm{T})_\mathrm{p}\right]\end{aligned}$$

With a little re-arrangement,

$$\begin{aligned}&\mathrm{H\,(aq;w_1\ kg)} = \\ &\mathrm{n_1\,H_1^*}(\ell) \\ &+\mathrm{n_j}\left[\mathrm{H_j^\infty}(\mathrm{aq}) - \mathrm{v\,R\,T^2}\,(\partial \ln\gamma_\pm/\partial\mathrm{T})_\mathrm{p} + \mathrm{v\,R\,T^2}\,(\partial\phi/\partial\mathrm{T})_\mathrm{p}\right]\end{aligned}$$

The terms within the brackets [….] define the apparent molar enthalpy of salt j in aqueous solution, $\phi\,(\mathrm{H}_j)$.

$$\mathrm{H\,(aq;w_1\ kg)} = \mathrm{n_1\,H_1^*}(\ell) + \mathrm{n_j}\,\phi\,(\mathrm{H_j})$$

$$\mathrm{limit\,(m_j \to 0)}\,\phi\,(\mathrm{H_j}) = \phi\,(\mathrm{H_j})^\infty = \mathrm{H_j^\infty}(\mathrm{aq})$$

By definition

$$\mathrm{L\,(aq;w_1\ kg)} = \mathrm{H\,(aq;w_1\ kg)} - \mathrm{H\,(aq;w_1\ kg;id)}$$

$$\mathrm{L_1(aq)} = \mathrm{H_1(aq)} - \mathrm{H_1^*}(\ell)$$

$$\mathrm{L_j(aq)} = \mathrm{H_j(aq)} - \mathrm{H_j^\infty(aq)}$$

$$\mathrm{L\,(aq;w_1\ kg)} = \mathrm{n_1\,L_1(aq)} + \mathrm{n_j\,L_j(aq)} = \mathrm{n_j}\,\phi\,(\mathrm{L_j})$$

Thus,

$$\mathrm{L\,(aq;w_1\ kg;id)} = 0$$

Equation (e) forms the basis of comments on changes in enthalpy when a salt solution is diluted by adding $\Delta\mathrm{n_1}$ moles of water(ℓ). Hence

$$\begin{aligned}\Delta_\mathrm{dil}\,\mathrm{H} = &[(\mathrm{n_1}\ +\Delta\mathrm{n_1})\ \mathrm{H_1^*}(\ell) + \mathrm{n_j}\,\phi\,(\mathrm{H_j} -\ \mathrm{final}\ )] \\ &-[\mathrm{n_1\,H_1^*}(\ell) + \mathrm{n_j}\,\phi\,(\mathrm{H_j} -\ \mathrm{initial}\ )] - \Delta\mathrm{n_1\,H_1^*}(\ell)\end{aligned}$$

Or,

$$\Delta_\mathrm{dil}\,\mathrm{H} = \mathrm{n_j}\ [\phi\,(\mathrm{H_j} -\ \mathrm{final}\ ) - \phi\,(\mathrm{H_j} -\ \mathrm{initial}\ )]$$

If in a given experiment where '$\mathrm{n}_j = 1\ \mathrm{mol}$' and $\Delta\mathrm{n_1}$ is large such that $\phi\,(\mathrm{H_j} -\ \mathrm{final}\ )$ equals $\phi\,(\mathrm{H_j} -\ \mathrm{final}\ )^\infty$, equation (k) is re-written as shown in equation (l). Then,

$$\Delta_\mathrm{dil}\,\mathrm{H\,(n_j = 1\ mol)} = -\,[\phi\,(\mathrm{H_j}) - \phi\,(\mathrm{H_j})^\infty]$$

Or,

$$\Delta_\mathrm{dil}\mathrm{H\,(n_j = 1\ mol)} = -\phi\,(\mathrm{L_j})$$

If for such a dilution, heat passes from the surroundings into the system , $\Delta_\mathrm{dil}\,\mathrm{H\,(n_j = 1\ mol)}$ is positive and $\phi\,(L_j)$ is negative. Thus direct calorimetric measurement of $\Delta_\mathrm{dil}\mathrm{H\,(n_j = 1\ mol)}$ yields the relative apparent molar enthalpy of the salt in solution at molality m_j.

However we need to comment in more detail on the analysis of heats of dilution for salt solutions. We envisage a situation where a calorimeter records the heat associated with dilution of a given salt solution from an initial molality $\mathrm{m_i}$ to a final molality $\mathrm{m_f}$. A data set often includes pairs of $\mathrm{m_i - m_f}$ values together with the accompanying enthalpy change, $\Delta\mathrm{H(\ old\ \to\ new\ )}$ which yields the difference in apparent molar enthalpies of the two salt solutions, cf. equation (k). Thus

$$\Delta H(\text{ old } \rightarrow \text{ new }) = n_j\,[\phi(H_j;\text{ new }) - \phi(H_j;\text{ old })]$$

Or,

$$[\phi(H_j;\text{ new }) - \phi(H_j;\text{ old })] = \Delta H(\text{ old } \rightarrow \text{ new })/n_j$$

We note that the molalities of the 'new' and 'old' solutions differ and therefore the contributions of ion-ion interactions to the apparent molar enthalpies differ. In the event that sufficient solvent is added that m_f is effectively zero, then $\phi(H_j;\text{ new })$ is the infinitely dilute property $\phi(H_j)^{\infty}$.

The excess enthalpy H^E is given by equation (p).

$$H^E = m_j\,\phi(L_j) = m_j\,[\phi(H_j) - \phi(H_j)^{\infty}]$$

For salt solutions H^E is not negligible as a consequence of intense ion-ion interaction. However in order to calculate H^E and hence obtain an indication of the strength of these interactions we return to equation (m) and note that experiment yields the difference between $\phi(H_j;\text{ new })$ and $\phi(H_j;\text{ old })$. Since there are no ion-ion interactions at infinite dilution, the difference $[\phi(H_j) - \phi(H_j)^{\infty}]\{\text{ i.e. }\phi(L_j)\}$ is obtained as a function of m_j(old).

A key component of the difference $[\phi(H_j;\text{ new }) - \phi(H_j;\text{ old })]$ is charge-charge interaction in the real solutions which is calculated using, for example, the Debye-Huckel equations. These equations start out with a relation between $\ln(\gamma_{\pm})$ where $\gamma_{\pm}$ is the mean ionic activity coefficient and I the ionic strength (or, in a simple solution, molality m_j). These equations are differentiated with respect to temperature (at fixed pressure) requiring therefore the corresponding dependences of molar volume $V_1^*(\ell)$ and relative permittivity $\varepsilon_r^*(\ell)$ of the solvent. Not surprisingly a large chemical literature describes a range of procedures for analysing the calorimetric results. In most cases the starting point is the Debye-Huckel Limiting Law.

For $Bu_4N^+Br^-(aq)$, the dependence of $\phi(L_j)$ on m_j was expressed [1] using equation (q). S_H was taken from the compilation published by Helgeson and Kirkham [2].

$$\phi(L_j) = S_H\,(m_j/m^0)^{1/2} + \sum B_i\,(m_j/m^0)^{(i+1)/2}$$

For $(HOC_2H_4)_4N^+Br^-(aq)$, an extended Debye –Huckel equation was used having the following form [3].

$$\phi(L_j) = S_H\,(m_j/m^0)^{1/2}\left[\frac{1}{1+(m_j/m^0)^{1/2}} - \frac{\sigma\,(m_j/m^0)^{1/2}}{3}\right] + B\,(m_j/m^0) + C\,(m_j/m^0)^{3/2}$$

The dependence of $\phi(L_j)$ on m_j for 1,1'-dimethyl-4,4'-dipyridinium dichloride(aq; 298 K) was expressed [3] using a simple polynomial in $(m_j/m^0)^{1/2}$.

The Pitzer equations describing the properties of salt solutions also provide a basis for examining the enthalpies of dilution of, for example [4], NaCl(aq). An interesting group of papers [5] compares relative apparent molar enthalpies of salts in D_2O and H_2O; i.e. $\phi(L_j;D_2O) - \phi(L_j;H_2O)$. The compositions of the salt solutions are expressed in aquamolalities; i.e. m_j moles of salt in 55.1 moles of solvent. The difference is expressed as a quadratic in aqueous molality using Kerwin's equation.

$$\phi(L_j;H_2O \rightarrow D_2O) = k_1\,m_j + k_2\,(m_j)^2$$

Further examples are listed in reference [6].

Footnotes

[1] J. E. Mayrath and R. H. Wood, J. Chem. Thermodyn., 1983,**15**,625; and references therein.

[2] H. C. Helgeson and D. H Kirkham, Am. J. Sci.,1974,**274**,1199.

[3] G. Perron and J. E. Desnoyers, J. Solution Chem.,1972,**1**,537.

[4] R. H. Busey, H. F. Holmes and R. E. Mesmer, J.Chem.Thermodyn., 1984,**16**, 343.

[5]

a. A. S. Levine and R. H. Wood, J.Phys.Chem.,1973,**77**,2390.

b. Y.-C. Wu and H.L.Friedman, J.Phys.Chem.,1966,**70**,166.
c. J. E. Desnoyers, R. Francescon, P. Picker and C. Jolicoeur, Can. J. Chem., 1971, **49**,3460

[6]

a. S. Lindenbaum, J.Chem.Thermodyn., 1971, **3**,625; J. Phys. Chem., 1971,**75**,3733; Na^+ and Bu_4N^+ salts of carboxylic acids(aq).
b. R. H. Wood and F. Belkin, J. Chem. Eng. Data, 1973, **18**,184; Extra \left or missing \right.
c. D. D. Ensor, H. L. Anderson and T. G. Conally, J. Phys. Chem.,1974,**78**,77.
d. D. D. Ensor and H. L. Anderson, J. Chem. Eng. Data, 1973, **18**,205; $NaCl(aq)$.
e. G. E. Boyd, J. W. Chase and F. Vaslow, J. Phys. Chem., 1967, **71**, 573; $R_4\ N^+X(aq)$.
f. S. Lindenbaum, J. Phys.Chem.,1969,**73**,4734; $[Bu_3\ N-(CH_2)_8-NBu_3]\ X_2$

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1.8.12: Enthalpies- Born-Bjerrum Equation- Salt Solutions

It is generally assumed that the Born Equation yields a difference in Gibbs energies rather than Helmholtz energies and so one can use the Gibbs-Helmholtz Equation for the dependence on temperature at fixed pressure to yield the Born-Bjerrum Equation, assuming that $(\mathrm{dr_j/dT})$ is zero.

$$\Delta(\mathrm{pfg \rightarrow s\,ln})\mathrm{H_j}\left(\mathrm{c_j = 1moldmdm^{-3}; id; T; p}\right) = \\ -\left[\mathrm{N_A}\ (\mathrm{z_j\,e})^2/8\,\pi\,\mathrm{r_j}\,\varepsilon_0\right]\ \left[1-(1/\varepsilon_\mathrm{r})-(\mathrm{T}/\varepsilon_\mathrm{r})\ (\partial \ln \varepsilon_\mathrm{r}/\partial \mathrm{T})_\mathrm{p}\right]$$

In fact an early calorimetric study showed that in terms of predicting the enthalpies of solution for salts, the Born equation is inadequate, often predicting the wrong sign. [1,2]

Differentiation of equation (a) with respect to temperature yields an equation for the partial molar isobaric heat capacity of ion j in a solution having ideal thermodynamic properties.

$$C_{pj}\left(\mathrm{sln}; c_j = 1\ \mathrm{moldm^{-3}; id; T; p}\right) \\ = -\left[\mathrm{N_A}\ (\mathrm{z_j\,e})^2/8\,\pi\,\mathrm{r_j}\,\varepsilon_0\right]\ \left[\partial\left\{(1/\varepsilon_\mathrm{r})+(\mathrm{T}/\varepsilon_\mathrm{r})\ \partial \ln \varepsilon_\mathrm{r}/\partial \mathrm{T}\right\}/\partial \mathrm{T}\right]$$

Footnotes

[1] F. A. Askew, E. Bullock, H. T. Smith, R. K. Tinkler, O. Gatty and J. H. Wolfenden, J. Chem. Soc., 1934, 1368.

[2] For estimation of single in enthalpies see M. Booij and G. Somsen, Electrochim Acta,1983,**28**,1883.

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1.8.13: Enthalpies- Liquid Mixtures

For an ideal binary liquid mixture the Gibbs energy at temperature T is given by equation (a).

$$\mathrm{G(mix;id)} = \mathrm{n_1}\ [\mu_1^*(\ell) + \mathrm{R\,T\ ln\,(x_1)}] + \mathrm{n_2}\ [\mu_2^*(\ell) + \mathrm{R\,T\ ln\,(x_2)}]$$

From the Gibbs-Helmholtz equation,

$$\mathrm{H(mix;id)} = \mathrm{n_1\,H_1^*}(\ell) + \mathrm{n_2\,H_2^*}(\ell)$$

Hence for an ideal binary liquid mixture,

$$\mathrm{H_1(mix;id)} = \mathrm{H_1^*}(\ell)\ \text{and}\ \mathrm{H_2(mix;id)} = \mathrm{H_2^*}(\ell)$$

The molar enthalpy of a real binary liquid mixture is given by equation (d).

$$\mathrm{H_m} = \mathrm{x_1\,H_1(mix)} + \mathrm{x_2\,H_2(mix)}$$

Therefore the molar enthalpy of mixing for a real binary liquid mixture is given by equation (e).

$$\Delta_{\mathrm{mix}}\,H_m = x_1\ [H_1(\mathrm{mix}) - H_1^*(\ell)] + x_2\ [H_2(\mathrm{mix}) - H_2^*(\ell]$$

Significantly equations (b) and (e) show that the molar enthalpy of mixing of an ideal binary liquid mixture, $\Delta_{\mathrm{mix}}\,H_m(\mathrm{id})$ is zero. The latter condition offers an important point of reference for isobaric calorimetry. [1] If we discover that the mixing of two liquids (at constant pressure) is not zero, the measured molar heat of mixing [$= \Delta_{\mathrm{mix}}\,\mathrm{H_m}$] is an immediate indicator of the extent to which the properties of a given mixture are not ideal.

Nevertheless it is important to set down a link between the measured enthalpies of mixing with the activity coefficients of two liquid components. To this end we start with the equation for the chemical potentials of liquid component 1 in a liquid mixture at temperature T and pressure p (which is close to ambient); equation (f).

$$\mu_1(\mathrm{mix}) = \mu_1^*(\ell) + \mathrm{R\,T\ ln\,(x_1\,f_1)}$$

where

$$\mathrm{limit}\,(x_1 \to 1)\ f_1 = 1\ \text{at all}\ T\ \text{and}\ p.$$

The Gibbs - Helmholtz equation yields an equation for the partial molar enthalpy of component 1 in the liquid mixture. Thus

$$\mathrm{H_1(mix)} = \mathrm{H_1^*}(\ell) - \mathrm{R\,T^2\ [\partial ln\,(f_1)\,/\partial T]_p}$$

Similarly,

$$\mathrm{H_2(mix)} = \mathrm{H_2^*}(\ell) - \mathrm{R\,T^2\ [\partial ln\,(f_2)\,/\partial T]_p}$$

Hence,

$$\mathrm{H_m(mix)} = \mathrm{H_m(mix;id)} - \mathrm{R\,T^2}\ \left\{\mathrm{x_1\ [\partial ln\,(f_1)\,/\partial T]_p} + \mathrm{x_2\ [\partial ln\,(f_2)\,/\partial T]_p}\right\}$$

We also obtain equations for the excess molar enthalpies of the two components (at defined T and p).

$$\mathrm{H_1^E(mix)} = -\mathrm{R\,T^2\ [\partial ln\,(f_1)\,/\partial T]_p}$$

and

$$\mathrm{H_2^E(mix)} = -\mathrm{R\,T^2\ [\partial ln\,(f_2)\,/\partial T]_p}$$

The excess molar enthalpy,

$$\mathrm{H_m^E(\ mix\ )} = -\mathrm{R\,T^2}\ \left\{\mathrm{x_1\ [\partial ln\,(f_1)\,/\partial T]_p} + \mathrm{x_2\ [\partial ln\,(f_2)\,/\partial T]_p}\right\}$$

At fixed pressure, the differential dependence of $\mathrm{H_m^E(mix)}$ on temperature yields the corresponding excess isobaric heat capacity of mixing.

Footnotes

[1] J. B. Ott and C. J. Wormald, Experimental Thermodynamics, IUPAC Chemical Data Series, No. 39, ed. K. N. Marsh and P. A. G. O'Hara, Blackwell, Oxford, 1994, chapter 8.

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SECTION OVERVIEW

1.9: Entropy

1.9.1: Entropy - Second Law of Thermodynamics

1.9.2: Entropy- Dependence on Temperature and Pressure

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1.9.1: Entropy - Second Law of Thermodynamics

A closed system (in addition to the thermodynamic energy U) is characterised by two functions of state.

1. Temperature, T: an intensive variable.
2. Entropy, S: an extensive variable.

The concept of entropy is particularly valuable in commenting on the direction of spontaneous chemical reaction [1].

The Second Law of Thermodynamics states that for spontaneous chemical reaction in a closed system [2].

$$\mathrm{T\,dS} = \mathrm{q} + \mathrm{A\,d}\xi$$

where

$$\mathrm{A\,d}\xi \geq 0$$

These two equations comprise the Second Law [3]. The product of the affinity for spontaneous chemical reaction and the extent of chemical reaction (i.e. accompanying change in composition) can never be negative. This is the thermodynamic `selection rule' for which there are absolutely no exceptions. Chemists base their analysis of chemical processes on the certainty of this rule (or axiom). The key point is the sense of direction of spontaneous change which emerges [4].

In the event that the affinity for spontaneous change is zero, no change in chemical composition occurs in a closed system; i.e. $\mathrm{d}\xi$ is zero and the rate of change $\mathrm{d}\xi/\mathrm{dt}$ is zero. The system and surroundings are in equilibrium. Hence

$$\mathrm{T\,dS} = \mathrm{q} \quad (\text{ at } \mathrm{A} = 0)$$

The latter equation has a particular set of applications. We imagine a closed system for which the affinity for spontaneous change is zero. We perturb the system by a change in pressure such that there is a corresponding change in composition-organisation in the system. However as we change the pressure along a certain pathway, we assert that the affinity for spontaneous change is always zero. Then between states I and II, at constant temperature T

$$\mathrm{T\,S(II)} - \mathrm{T\,S(I)} = \mathrm{T} \int_{\text{statel}}^{\text{state II}} \mathrm{dS} = \mathrm{q}$$

The pathway between these two states is called reversible or an equilibrium transformation. In fact the change in pressure must be carried out infinitely slowly because we must allow the chemical composition/molecular organisation to hold to the condition that there is no affinity for spontaneous change.

All processes in the real world (i.e. all natural processes) are irreversible; there is a defined direction for spontaneous changes [5].

Footnotes

[1] Many authors offer an explanation of the property, entropy. One view is that to attempt an explanation of the "meaning" of entropy is a complete waste of time (M. L. McGlashan, J. Chem. Educ., 1966,**43**, 226). A wide-ranging discussion is given by P.L. Huyskens and G.G. Siegel,Bull. Soc.Chem.Belg., 1988,**97**, 809, 815 and 823.

E.A. Guggenheim [Thermodynamics, North-Holland, Amsterdam, 1950]. This monograph is often cited for the following bold statement (page 11): "There exists a function S of the state of a system called the **entropy** of the system .....".

H. Margenau [The Nature of Physical Reality, McGraw-Hill, New York, 1950] states 'Entropy is as definite and clear a thing as other thermodynamic quantities'.

The common view in introductory chemistry textbooks for many years has been that entropy is a measurement of randomness and/or disorder. However this view is unhelpful if not meaningless [E. T. Jaynes, Am. J.Phys.,1965,**33**,391; F. L. Lambert, J. Chem. Educ.,1999,**76**,1385; 2002,**79**,187.] indeed a myth [W Brostow, Science 1972,**178**,211.] and an educational disaster [M. Sozlibir, J.K.Bennett, J. Chem. Educ.,2007,84,1204.]

The generally accepted view [F. L. Lambert, J.Chem.Educ.,2002,**79**,1241] is that an entropy increase results from the energy of molecular motion becoming more dispersed or 'spread out'; e.g. in the two classic examples of a system being warmed by hotter surroundings or, isothermally, when a system's molecules have greater volume for their energetic movement the energy of

molecular motion becoming more dispersed or ‘spread out’; e.g. in the two classic examples of as system being warmed by hotter surroundings or, isothermally, when a system’s molecules have greater volume for their energetic movement. The concept is exceptionally valuable because entropy increase can be seen by chemists as simply involving the energy associated with mobile molecules spreading out more in three-dimensional space, whether a new total system of ‘less hot plus once-cooler’ or isothermally in a larger volume. This simple view is equivalent to the dispersal of energy in *phase* space. In quantum mechanical terms, ’energy dispersal’ means that a system will come to equilibrium in a final state that is optimal because it affords a maximal number of accessible energy arrangements. Even though the system can be in only one arrangement at one instant, its energy is truly dispersed because at the next instant it can be in a different arrangement: this amounts to a ‘temporal dance’ over a very small fraction of the hyper-astronomical number of microstates predicted by the Boltzmann relation. The account given here is based on a written comments in correspondence from F. L. Lambert.

[2] From equation (a), $\mathrm{T.\ dS} = [\mathrm{K}] - \left[\mathrm{JK^{-1}}\right] = [] + \left[\mathrm{Jmol^{-1}}\right] = [\mathrm{J}]$

[3] Equations (a) and (b) can be re-expressed in terms of the contribution to the change in entropy dS by a process (e.g. chemical reaction) within the system $\mathrm{d_iS}$. Then

$$\mathrm{T\,dS} = \mathrm{q} + \mathrm{T\,d_sS}$$

where

$$\mathrm{d_iS} > 0$$

Equation (B) is the Second Law in that $\mathrm{d_iS}$ cannot be negative. For a reversible process $\mathrm{d_iS} = 0$. But for all processes in the real world, $\mathrm{d_iS}$ is positive. In other words all spontaneous processes occur in the direction whereby there is a positive contribution from $\mathrm{d_iS}$ to the change in entropy dS.

[4] This concept of spontaneous change, coupled with the idea that changes occur in a predefined direction is linked with the idea that time is "one-sided". (a) I. Prigogine, From Being to Becoming, Freeman, San Francisco, 1980, page 6. (b) see also G. Nicolis and I. Prigogine, Self-Organization in Non-Equilibrium Systems, Wiley, New York, 1977.

[5] Equation (a) forms the basis of an oft-quoted comment. For an isolated system, q is zero. Then $\mathrm{T\,dS} = \mathrm{A\,d\xi}$ where $\mathrm{A\,d\xi} \geq 0$

So for all spontaneous processes in an isolated system, $\mathrm{dS} > 0$. This is the basis of the statement that the entropy of the universe is increasing if the universe can be treated as an isolated system. But these comments stray from immediate interests of chemists.

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1.9.2: Entropy- Dependence on Temperature and Pressure

The volume of a given closed system at equilibrium prepared using n_1 moles of solvent (water) and n_j moles of solute-j is defined by the set of independent variables shown in equation (a).

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \mathrm{A} = 0, \xi^{\mathrm{eq}}\right]$$

The same set of independent variables defines the entropy S.

$$\mathrm{S} = \mathrm{S}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \mathrm{A} = 0, \xi^{\mathrm{eq}}\right]$$

We envisage that the system is displaced by a change in pressure along a path where the system remains at equilibrium (i.e. $\mathrm{A} = 0$) and the volume remains the same as defined by equation (a). In a plot of entropy against p, the gradient of the plot at the point defined by the independent variables, $[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \mathrm{A} = 0, \boldsymbol{\xi}^{\mathrm{eq}}]$ is given by equation (c).

Isochoric

$$\left(\frac{\partial S}{\partial p}\right)_{V,A=0}$$

The set of derivatives is completed by the following partial derivatives.

Isothermal

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{T,A=0}}$$

Isobaric

$$\left(\frac{\partial S}{\partial T}\right)_{p,A=0}$$

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1.9.3: Entropy and Spontaneous Reaction

It is often stated that the entropy of a system is a maximum at equilibrium. This is not generally true and is certainly not the case for closed systems at either (a) fixed T and p, or (b) fixed T and V.

We rewrite the **Master Equation** in the following way:

$$\mathrm{dS} = (1/\mathrm{T})\,\mathrm{dU} + (\mathrm{p}/\mathrm{T})\,\mathrm{dV} + (\mathrm{A}/\mathrm{T})\,\mathrm{d}\xi;\ \mathrm{A}\,\mathrm{d}\xi \geq \text{ zero}$$

Temperature T is positive and non-zero. At constant energy and constant volume (i.e. isoenergetic and isochoric), spontaneous processes are accompanied by an increase in entropy. This statement is important in statistical thermodynamics where the condition, 'constant U and constant V' is important.

The following equation defines the enthalpy H of a closed system.

$$\mathrm{H} = \mathrm{U} + \mathrm{p}\,\mathrm{V}$$

Then

$$\mathrm{dU} = \mathrm{dH} - \mathrm{p}\,\mathrm{dV} - \mathrm{V}\,\mathrm{dp}$$

From equation (a),

$$\mathrm{dS} = (1/\mathrm{T})\,\mathrm{dH} - (\mathrm{p}/\mathrm{T})\,\mathrm{dV} - (\mathrm{V}/\mathrm{T})\,\mathrm{dp} + (\mathrm{p}/\mathrm{T})\,\mathrm{dV} + (\mathrm{A}/\mathrm{T})\,\mathrm{d}\xi \text{ with } \mathrm{A}\,\mathrm{d}\xi \geq \text{ zero}$$

Hence,

$$\mathrm{dS} = (1/\mathrm{T})\,\mathrm{dH} - (\mathrm{V}/\mathrm{T})\,\mathrm{dp} + (\mathrm{A}/\mathrm{T})\,\mathrm{d}\xi;\ \mathrm{A}\,\mathrm{d}\xi \geq \text{ zero}$$

Temperature T is always positive. Hence at constant enthalpy and pressure (i.e. iso-enthalpic and isobaric) all spontaneous processes produce an increase in entropy.

We have identified two sets of conditions under which an increase in entropy accompanies a spontaneous process. If we follow through a similar argument with respect to the Gibbs energy, the outcome is not straightforward. By definition,

$$\mathrm{G} = \mathrm{H} - \mathrm{T}\,\mathrm{S}$$

Then

$$\mathrm{dG} = \mathrm{dH} - \mathrm{T}\,\mathrm{dS} - \mathrm{S}\,\mathrm{dT}$$

Or,

$$\mathrm{S} = -\mathrm{dG}/\mathrm{dT} + \mathrm{dH}/\mathrm{dT} - \mathrm{T}\,\mathrm{dS}/\mathrm{dT}$$

But from equation (e)

$$\mathrm{dH}/\mathrm{dT} = \mathrm{T}\,\mathrm{dS}/\mathrm{dT} + (\mathrm{V}/\mathrm{T})\,\mathrm{dp}/\mathrm{dT} - (\mathrm{A}/\mathrm{T})\,\mathrm{d}\xi/\mathrm{dT}$$

Hence,

$$\mathrm{S} = -(\mathrm{dG}/\mathrm{dT}) + \mathrm{V}\,(\mathrm{dp}/\mathrm{dT}) - \mathrm{A}\,(\mathrm{d}\xi/\mathrm{dT}) \text{ with } \mathrm{A}\,\mathrm{d}\xi \geq \text{ zero}$$

Clearly no definite conclusions can be drawn about changes in entropy S under isobaric - isothermal conditions. We stress these points because again it is often tempting to link, misguidedly, entropies to the degree of 'muddled-up-ness'. This is the basis of many explanations of entropy. For example, neither the volume nor energy of a deck of cards change on shuffling. Whether what actually happens on shuffling a new well-ordered deck of cards clarifies the meaning of entropy seems doubtful.

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1.9.4: Entropy- Dependence on Temperature

Using a calculus operation, the isochoric dependence of entropy of temperature is related to the corresponding isobaric dependence. Thus

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

But

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Hence,

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{p}} + \left(\frac{\partial \mathrm{p}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \left[\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}\right]^2$$

Or,

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_p - \frac{(E_p)^2}{K_T}$$

The final term in equation (c) contains the variable $\mathrm{p} - \mathrm{V} - \mathrm{T}$.

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1.9.5: Entropies- Solutions- Limiting Partial Molar Entropies

A key equation relates the chemical potential and partial molar entropy of solute-j. For a given solute j in an aqueous solution,

$$\mathrm{S_j(aq) = -\left[\partial \mu_j(aq)/\partial T\right]_p}$$

In order to appreciate the importance of equation (a) we initially confine our attention to the properties of a solution whose thermodynamic properties are ideal. A given aqueous solution contains solute j at temperature T and ambient pressure (which is close to the standard pressure).

$$\mathrm{\mu_j(aq; id; T; p) = \mu_j^0(aq; T; p) + R\,T\,\ln\left(m_j/m^0\right)}$$

Using equation (a),

$$\mathrm{S_j(aq; id; T; p) = S_j^0(aq; T; p) - R\,\ln\left(m_j/m^0\right)}$$

$\mathrm{S_j^0(aq; T; p)}$ is the partial molar entropy of solute j in an ideal aqueous solution having unit molality [1,2]. Therefore for both real and ideal solutions [3],

$$\mathrm{limit}\,(m_j \to 0)\, S_j(aq; T; p) = +\infty$$

In other words the limiting partial molar entropy for solute j is infinite. Interestingly if the aqueous solution contains two solutes j and k, then the following condition holds for solutions at temperature T and pressure p.

$$\mathrm{limit\,(m_j \to 0; m_k \to 0)\,[S_j(aq; T; p) - S_k(aq; T; p)] = S_j^0(aq) - S_k^0(aq)}$$

Similarly

$$\mathrm{limit\,(m_j \to 0; m_k \to 0)\,[\mu_j(aq; T; p) - \mu_k(aq; T; p)] = \mu_j^0(aq) - \mu_k^0(aq)}$$

The partial molar entropy of solute j in a real solution is given by equation (g).

$$S_j(aq; T; p) = \\ S_j^0(aq; T; p) - R\,\ln\left(m_j/m^0\right) - R\,\ln\left(\gamma_j\right) - RT\left[\frac{\partial \ln\left(\gamma_j\right)}{\partial T}\right]_p$$

A given aqueous solution having thermodynamic properties which are ideal contains a solute j, molality $\mathrm{m_j}$. The partial molar entropy of the solvent is given by equation (h).

$$\mathrm{S_1(aq; id; T; p) = S_1^*(\ell; T; p) + R\,M_1\,m_j}$$

Hence,

$$\mathrm{limit\,(m_j \to 0)\,S_1(aq; id; T; p) = S_1^*(\ell; T; p)}$$

When an ideal solution is diluted the partial molar entropy of the solvent approaches that of the pure solvent.

A given aqueous solution is prepared using $1\ \mathrm{kg}$ of solvent and $\mathrm{m_j}$ moles of solute j at temperature T and pressure p, the latter being close to the standard pressure. The entropy of the solution is given by equation (j).

$$\mathrm{S\,(aq; w_1 = 1\ kg) = M_1^{-1}\,S_1(aq) + m_j\,S_j(aq)}$$

In the event that the thermodynamic properties of the solution are ideal the entropy of the solution is given by equation (k).

$$\mathrm{S\,(aq; id; w_1 = 1\ kg) = \\ M_1^{-1}\,\left[S_1^*(\ell) + R\,M_1\,m_j\right] + m_j\,\left[S_j^0(aq) - R\,\ln\left(m_j/m^0\right)\right]}$$

Interestingly,

$$\mathrm{limit\,(m_j \to 0)\,S\,(aq; id; w_1 = 1\ kg) = \\ M_1^{-1}\,S_1^*(\ell) + (0)\,\left[S_j^0(aq) - R\,\ln\left(0/m^0\right)\right]}$$

But

$$\text{limit}\,(\mathrm{m_j} \to 0)\,\mathrm{m_j}\,\ln\left(\mathrm{m_j}/\mathrm{m}^0\right) = 0$$

In other words the entropy for an ideal solution in the limit of infinite dilution is given by the entropy of the pure solvent. For a real solution,

$$\mathrm{S_1(aq;T;p)} = \mathrm{S_1^*}(\ell;\mathrm{T;p}) + \phi\,\mathrm{R\,M_1\,m_j} + \mathrm{R\,T\,M_1\,m_j}\left(\frac{\partial\phi}{\partial\mathrm{T}}\right)_\mathrm{p}$$

Hence,

$$\begin{aligned}&\mathrm{S\,(aq;w_1 = 1\ kg;T;p)}\\ &= \mathrm{M_1^{-1}}\left[\mathrm{S_1^*}(\ell;\mathrm{T;p}) + \phi\,\mathrm{R\,M_1\,m_j} + \mathrm{R\,T\,M_1\,m_j}\left(\frac{\partial\phi}{\partial\mathrm{T}}\right)_\mathrm{p}\right]\\ &\quad+\mathrm{m_j}\left[\mathrm{S_j^0(aq;T;p)} - \mathrm{R}\,\ln\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right) - \mathrm{R\,T}\left(\frac{\partial\ln\left(\gamma_\mathrm{j}\right)}{\partial\mathrm{T}}\right)_\mathrm{p}\right]\end{aligned}$$

The difference $[\mathrm{S\,(aq;w_1 = 1\ kg;T;p)} - \mathrm{S\,(aq;id;w_1 = 1\ kg;T;p)}]$ yields the excess entropy, $\mathrm{S^E\,(aq;w_1 = 1\ kg;T;p)}$.

Footnotes

[1] For a salt solution, the standard partial molar entropy of the salt is given by the sum of standard partial molar entropies of the ions. For a 1:1 salt, $S_j^0(aq) = S_+^0(aq) + S_-^0(aq)$

[2] Y. Marcus and A. Loewenschuss, Annu. Rep. Prog. Chem., Ser. C, Phys. Chem., 1984, **81**, chapter 4.

[3] For comments on the entropy of dilution of salt solutions see (a classic paper), H. S. Frank and A. L. Robinson, J. Chem. Phys.,1940,**8**,933.

[4] For comments on partial molar entropies of apolar solutes in aqueous solutions see, H. S. Frank and F. Franks, J. Chem. Phys.,1968,**48**,4746.

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1.9.6: Entropies- Liquid Mixtures

The chemical potential of liquid component 1 in a binary liquid mixture (at temperature T and pressure p, close to the standard pressure p^o) is related to the mole fraction x_1 using equation (a).

$$\mu_1(\mathrm{mix};\mathrm{id}) = \mu_1^*(\ell) + \mathrm{R}\,\mathrm{T}\,\ln(\mathrm{x}_1)$$

But

$$\mathrm{S}_1(\mathrm{mix}) = -\left[\partial\mu_1(\mathrm{mix})/\partial\mathrm{T}\right]_\mathrm{p}$$

Then,

$$\mathrm{S}_1(\mathrm{mix};\mathrm{id}) = \mathrm{S}_1^*(\ell) - \mathrm{R}\,\ln(\mathrm{x}_1)$$

Hence the molar entropy of mixing of an ideal binary liquid mixture (at defined T and p) is given by Equation 1.9.6.1.

$$\Delta_{\mathrm{mix}}\,S_m(\ \mathrm{id}\ ) = -R\,[x_1\,\ln(x_1) + x_2\,\ln(x_2)] \tag{1.9.6.1}$$

The chemical potential of component 1 in a real binary liquid mixture (at temperature T and pressure p, near the standard pressure) is given by Equation 1.9.6.2.

$$\mu_1(\mathrm{mix}) = \mu_1^*(\ell) + \mathrm{R}\,\mathrm{T}\,\ln(\mathrm{x}_1\,\mathrm{f}_1) \tag{1.9.6.2}$$

Then

$$\mathrm{S}_1(\mathrm{mix}) = \mathrm{S}_1^*(\ell) - \mathrm{R}\,\ln(\mathrm{x}_1) - \mathrm{R}\,\ln(\mathrm{f}_1) - \mathrm{R}\,\mathrm{T}\,\left[\partial\ln(\mathrm{f}_1)/\partial\mathrm{T}\right]_\mathrm{p}$$

$$S_1(\mathrm{mix}) = S_1(\mathrm{mix};\ \mathrm{id}\ ) - R\,\ln(f_1) - RT\,\left[\partial\ln(f_1)/\partial T\right]_p$$

Similarly,

$$\mathrm{S}_2(\mathrm{mix}) = \mathrm{S}_2(\mathrm{mix};\mathrm{id}) - \mathrm{R}\,\ln(\mathrm{f}_2) - \mathrm{R}\,\mathrm{T}\,\left[\partial\ln(\mathrm{f}_2)/\partial\mathrm{T}\right]_\mathrm{p}$$

The extent to which the partial molar entropies for each liquid component in a given liquid mixture differs from that in the corresponding ideal mixture depends on the rational activity coefficient and its dependence on temperature. Hence we define excess partial molar entropies for both liquid components.

$$S_1^E = -R\,\ln(f_1) - RT\,\left[\partial\ln(f_1)/\partial T\right]_p$$

and

$$S_2^E = -R\,\ln(f_2) - RT\,\left[\partial\ln(f_2)/\partial T\right]_p$$

For the binary mixture,

$$S_m^E = -R\{x_1\,\ln(f_1) + x_1\,\left[\partial\ln(f_1)/\partial T\right]_p + x_2\,\ln(f_2) + x_2\,\left[\partial\ln(f_2)/\partial T\right]_p\}$$

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1.10: Gibbs Energies

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1.10.1: Gibbs Energy

The Gibbs energy is an extensive state variable defined by the following equation.

$$\mathrm{G} = \mathrm{U} + \mathrm{p}\,\mathrm{V} - \mathrm{T}\,\mathrm{S}$$

Instead of Gibbs energy the terms Gibbs free energy and Gibbs function are often used. Physicists prefer the term Gibbs function [1]. The term ‘free energy’ is not encouraged. Everyday experience tells us that no energy is ‘free’.

Footnote

[1] Nevertheless the French term ‘enthalpie libre’ (i.e. free enthalpy) for G has merit. Enthalpy is defined by $\mathrm{H} = \mathrm{U} + \mathrm{pV}$. Then $\mathrm{G} = \mathrm{H}–\mathrm{TS}$. The product TS is the linked energy in a system from which no work can be produced. Hence the available or ‘free’ part of the enthalpy is the Gibbs energy.

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1.10.2: Gibbs Energy- Thermodynamic Potential

The Gibbs energy of a system,

$$\mathrm{G} = \mathrm{U} + \mathrm{p}\,\mathrm{V} - \mathrm{T}\,\mathrm{S}$$

For a closed single phase system, changes in thermodynamic energy dU and Gibbs energy dG are related by the following equation.

$$\mathrm{dG} = \mathrm{dU} + \mathrm{p}\,\mathrm{dV} + \mathrm{V}\,\mathrm{dp} - \mathrm{T}\,\mathrm{dS} - \mathrm{S}\,\mathrm{dT}$$

The change in thermodynamic energy dU is related to the affinity for spontaneous change using the Master Equation.

$$\mathrm{dU} = \mathrm{T}\,\mathrm{dS} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi; \quad \mathrm{A}\,\mathrm{d}\xi \geq 0$$

We use equation (b) by substituting for dU in equation (a). Hence,

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} - \mathrm{A}\,\mathrm{d}\xi; \quad \mathrm{A}\,\mathrm{d}\xi \geq 0$$

Chemists carry out most of their experiments under the twin conditions, constant pressure (usually ambient) and constant temperature (often near room temperature). Hence we can see why the latter equation is so important. At fixed T and p,

$$\mathrm{dG} = -\mathrm{A}\,\mathrm{d}\xi; \quad \mathrm{A}\,\mathrm{d}\xi \geq 0$$

Hence under common laboratory conditions the direction of spontaneous change (e.g. chemical reaction) is in the direction for which G decreases. The spontaneous 'flow' of a chemical reaction (at fixed T and p) is down the plot of G against extent of reaction, ξ; high to low G. This statement opens the door to the quantitative study of chemical reactions. Thus from equation (e),

$$\mathrm{A} = -\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{\mathrm{T,p}}$$

The Gibbs energy decreases until the affinity for spontaneous change is zero; i.e. equilibrium. Then,

$$\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)^{\mathrm{eq}}_{\mathrm{t,p}} = 0$$

At equilibrium the Gibbs energy is a minimum [1]. In general terms, a thermodynamic potential is an extensive property of a closed system which reaches an extremum at equilibrium under specified conditions. For processes in closed systems at fixed T and p, the thermodynamic potential is G. Thus T and p are the natural variables for G.

Experience shows that for a given system there is one unique composition which corresponds to the minimum in Gibbs energy (at fixed T and p). In fact chemistry would be a very difficult subject (and it is difficult as it is) if there were many minima such that it was just a matter of chance which minimum a system ended up in following spontaneous chemical reaction.

The conclusions advanced above refer to the Gibbs energy of a closed system; i.e. a macroscopic property. We cannot at this stage draw conclusions about the properties of the chemical substances making up the system. At the molecular level a whole range of processes may be taking place; chemical reaction, diffusion, molecular collisions. We cannot comment on these using equation (g). It may be that one or more of these processes contributes towards an increase in Gibbs energy. However these processes operate in such a way that the fluctuations in Gibbs energies in small domains are opposed, holding the overall system at a minimum in G.

The Gibbs energy is a contrived property. It is not the 'energy' of the system. Nevertheless we can begin to 'understand' this property by returning to equation (d). Consider a system at equilibrium and at constant temperature ; i.e. $\mathrm{A} = 0$\) and $\mathrm{dT} = 0$. Then

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,A=0}$$

The familiar property, volume, is the differential dependence of Gibbs energy on pressure at constant temperature and at equilibrium. If we can assume that the coffee mug on this desk is at equilibrium, although I do not know (and can never know) its Gibbs energy, I know that the volume offers a direct measure of the dependence of its Gibbs energy on pressure. Indeed the link between a property which can be readily measured (e.g. volume or density) offers chemists a pathway into the Gibbs energy and a detailed thermodynamic analysis.

Footnote

[1] G. Willis and D. Ball, J.Chem.Educ.,1984,**61**,173.

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1.10.3: Gibbs Energies- Solutions- Solvent and Solute

A given solution (at temperature T and pressure p, where the latter is close to the standard pressure) is prepared using $1\ \mathrm{kg}$ of water and $\mathrm{m_j}$ moles of a simple solute. We consider the differential dependence of the excess Gibbs energy for the solution $\mathrm{G^E}$ on molality $\mathrm{m_j}$.

$$\mathrm{G^E_m = R\,T\,m_j\ [1 - \phi + \ln(\gamma_j)]}$$

Hence, at fixed T and p,

$$\mathrm{(1/R\,T)\ \left[dG^E/dm_j\right] = [1 - \phi + \ln(\gamma_j)] - m_j\ [d\phi/dm_j] + m_j\ [d\ln(\gamma_j)/dm_j]}$$

But according to the Gibbs-Duhem equation,

$$\mathrm{-\phi - m_j\ [d\phi/dm_j] + 1 + m_j\ [d\ln(\gamma_j)/dm_j] = 0}$$

Hence, we obtain an equation for $\ln(\gamma_j)$ as a function of the differential dependence of $\mathrm{G^E}$ on $\mathrm{m_j}$.[1]

$$\mathrm{\ln(\gamma_j) = (1/R\,T)\ \left[dG^E/dm_j\right]}$$

If we substitute for $\ln(\gamma_j)$ in the equation for $\mathrm{G^E}$, an equation for ϕ in terms of $\mathrm{G^E}$ is obtained.

$$\mathrm{1 - \phi = (1/R\,T)\ \left[G^E/m_j - dG^E/dm_j\right]}$$

A more elegant derivation of equation (e) starts out with the equation (a) for the excess Gibbs energy written in the following form.

$$\mathrm{\left[G^E/m_j\right]/R\,T = 1 - \phi + \ln(\gamma_j)}$$

Then at fixed T and p,

$$\mathrm{(1/R\,T)\ \left\{d\left[G^E/m_j\right]/dm_j\right\} = -(d\phi/dm_j) + d\ln(\gamma_j)/dm_j}$$

But according to the Gibbs-Duhem equation,

$$\mathrm{-(d\phi/dm_j) + (d\ln(\gamma_j)/dmm_j) = (\phi - 1)/m_j}$$

Then,

$$\mathrm{1 - \phi = -(1/R\,T)\ \left\{d\left[G^E/m_j\right]/dm_j\right\}\ m_j}$$

Or,

$$\mathrm{1 - \phi = -(1/R\,T)\ \left[dG^E/dm_j\right]\ m_j}$$

The latter equation does not however require that $(1 - \phi)$ is a linear function of $\mathrm{m_j}$. The actual form of this dependence has to be obtained by experiment.

Footnotes

[1] $\mathrm{\ln(\gamma_j) = \left[JK^{-1}\ mol^{-1}\right]^{-1}\left[K^{-1}\ \left[Jkg^{-1}\right]\ \left[molkg^{-1}\right]^{-1} = [1]\right.}$

[2] $\mathrm{(1 - \phi) = \left[\frac{1}{[\,J\ K^{-1}\ mol^{-1}]\ [K]}\right]\left[\frac{[Jkg^{-1}]}{[molkg^{-1}}} + \frac{[Jkg^{-1}]}{[molkg^{-1}]}\right] = [1]$

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1.10.4: Gibbs Energies- Equilibrium and Spontaneous Change

The Gibbs energy of a closed system at temperature T is related to the enthalpy H using equation (a) [1].

$$\mathrm{G} = \mathrm{H} - \mathrm{T}\,\mathrm{S}$$

The differential change in Gibbs energy at constant temperature is related to the change in enthalpy dH using equation (b).

$$\mathrm{dG} = \mathrm{dH} - \mathrm{T}\,\mathrm{dS}$$

For a process taking place in a closed system involving a change from state I to state II, the change in Gibbs energy is given by equation (c).

$$\Delta\mathrm{G} = \Delta\mathrm{H} - \mathrm{T}\,\Delta\mathrm{S}$$

The latter equation signals how changes in enthalpy and entropy determine the change in Gibbs energy. A given closed system at temperature T and pressure p is prepared using n_1 moles of solvent (water) and n_j moles of solute j. The system is at equilibrium such that the composition/organisation is represented by \(\xi^{\mathrm{eq}}\) and the affinity for spontaneous change is zero. We summarise this state of affairs as follows.

$$\mathrm{G}^{eq} = \mathrm{G}^{\mathrm{eq}}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \xi^{\mathrm{eq}}, \mathrm{A} = 0\right]$$

In a plot of G against ξ (at fixed T and p) the Gibbs energy is a minimum at ξ^{eq} [2]. The enthalpy H^{eq} of the equilibrium state can be represented in a similar fashion.

$$\mathrm{H}^{eq} = \mathrm{H}^{eq}\left[\ \mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \xi^{\mathrm{eq}}, \mathrm{A} = 0\right]$$

However it is unlikely that H^{eq} at ξ^{eq} corresponds to a minimum in enthalpy H when H is plotted as a function of ξ. A similar comment applies to the entropy S^{eq};

$$\mathrm{S}^{\mathrm{eq}} = \mathrm{S}^{\mathrm{eq}}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \xi^{\mathrm{eq}}, \mathrm{A} = 0\right]$$

However taken together H^{eq} and S^{eq} produce the minimum in G at G^{eq}.

$$\mathrm{G}^{\mathrm{eq}} = \mathrm{H}^{\mathrm{eq}} - \mathrm{T}\,\mathrm{S}^{\mathrm{eq}}$$

In summary; at thermodynamic equilibrium

i. A is zero,
ii. G is a minimum and
iii. the rate of change of composition/organisation $\mathrm{d}\xi/\mathrm{dt}$ is zero.

The latter condition emerges from the conclusion that this rate is zero if there is no affinity for change. For a given system at defined T and p, the state for which G is a minimum is unique [3]. Indeed if this was not the case, chemistry would be a very difficult subject. In a given spontaneous chemical reaction proceeds until the composition/organisation reaches ξ^{eq}. In other words the Gibbs energy is the important thermodynamic potential, certainly forming the basis of treatments of chemical reactions in closed systems at fixed T and p [4]. However a word of caution is in order. The Gibbs energy of a system differs from the thermodynamic energy U. In fact the Gibbs energy is a somewhat contrived property but aimed at a description of closed systems at fixed T and p. Nevertheless the Gibbs energy can be given practical significance. We consider a system at equilibrium (i.e. $\mathrm{A} = 0$) at temperature T and pressure p where in this state (state I) the Gibbs energy is $\mathrm{G}[\mathrm{I}]$. The system is displaced by a change in pressure to a neighbouring equilibrium state (at constant T). The equilibrium isothermal dependence of Gibbs energy $\mathrm{G}[\mathrm{I}]$ on pressure equals the volume of the system, $\mathrm{V}[\mathrm{I}]$ [5].

$$V = \left[\frac{\partial G}{\partial p}\right]_{T,A=0}$$

In other words we may not know the Gibbs energy of a system (in fact never know) at least we know that the pressure dependence is the volume which we can readily measure. The isobaric dependence of $\mathrm{G}[\mathrm{I}]$ on temperature for an equilibrium displacement yields the entropy.

$$S = -\left[\frac{\partial G}{\partial T}\right]_{p,A=0}$$

Four key points can be made.

i. The equilibrium state for a system at constant T and p corresponds to a minimum in Gibbs energy.
ii. The minimum in Gibbs energy of a given system is unique.
iii. In the non-equilibrium, there is no direct relationship between the gradient $(\partial G/\partial \xi)$ and the rate of spontaneous change, $(\partial \xi/\partial t)$.
iv. The equilibrium state is stable; $(\partial A/\partial \xi) < 0$ at ξ^{eq} [6].

Footnotes

[1]

$$G = [J]; T\,S = [K]\ \left[JK^{-1}\right] = [J]; p\,V = \left[Nm^{-2}\right]\ \left[m^3\right] = [Nm] = [J]$$
$$A\,\xi = \left[Jmol^{-1}\right]\ [mol] = [J]$$

[2] See for example

a. G. Willis and D. Ball, J. Chem. Educ.,1984, **61**, 173, and
b. P. L. Corio, J. Phys. Chem.,1983, **87**, 2416.

[3] This point is discussed in the monograph, F. Van Zeggeren and S. H. Story, The Computation of Chemical Equilibria, Cambridge University Press, 1970.

[4] The dependence of rate of reaction on composition is described using the law of mass action and rate constants. The law of mass action is in these terms, extrathermodynamic , meaning that the law does not follow from the first and second laws.

[5] For completeness we consider the case where in equilibrium state [I] at $\xi^{eq}[I]$, the system is displaced by a change to a neighbouring state having the same composition/organisation, $\xi[I]$; i.e. the system is 'frozen'. The isothermal dependence of $G[I]$ on pressure at constant composition equals the volume. Thus, $V[I] = \left[\frac{\partial G}{\partial p}\right]_{T,\xi[I]}$ Similarly, $S[I] = -\left[\frac{\partial G}{\partial T}\right]_{p,\xi[I]}$

The identities of S and V at constant '$A = 0$' and at $\xi^{eq}[I]$ arise from the fact that V and S are strong state variables.

[6] Consider a simple cup in which we have placed (delicately) a steel ball near the top edge.

i. We release the ball, the ball rolls down and the ball gathers speed.
ii. At the bottom of the cup the speed of the ball is a maximum (i.e. maximum in kinetic energy) where the potential energy is a minimum.
iii. The ball continues through the bottom of the cup and rises to the opposite edge.
iv. The ball slows down and then changes direction, falling back to the bottom of the cup.
v. If the surface of the cup is perfectly smooth (i.e. no energy lost to friction), the ball oscillates about the bottom of the well of the cup. This mechanical model is not correct for chemical reactions in closed systems. In fact the rate of the chemical reaction decreases as a system approaches the minimum in Gibbs energy.

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1.10.5: Gibbs Energies- Raoult's Law

We consider a closed system containing a (homogeneous) mixture of two volatile liquids. The closed system is connected to a pressure measuring device which records that at temperature T the pressure inside the closed system is $\mathrm{p(tot)}$. The composition of the liquid mixture is assayed; the mole fractions of the two components of the liquid are $\mathrm{x_1}$ and $\mathrm{x_2}$ (where $\mathrm{x_2 = 1–x_1}$). Thus the system contains two components so that in terms of the Phase Rule, $\mathrm{C = 2}$. There are two phases, vapour and liquid, so P equals 2. Thus in terms of the Rule, $\mathrm{P + F = C + 2}$, we have fixed the composition and the temperature using up the two degrees of freedom. Hence the pressure $\mathrm{p(tot)}$ is fixed.

The foundation of thermodynamics is experiment. So, in considering the properties of water in dilute aqueous solutions, we take account of the observation that the equilibrium vapour pressure $\mathrm{p_1^{eq}(aq)}$ of water in equilibrium with water in an aqueous solution (at fixed temperature) is approximately a linear function of the mole fraction of water in the solution; equation (a).

$$\mathrm{p_1^{eq}(aq) \cong p_1^*(\ell)\, x_1}$$

Thus as mole fraction $\mathrm{x_1}$ approaches unity (the composition of the solution approaches pure water where $\mathrm{x_1}$ is unity), the equilibrium vapour pressure $\mathrm{p_1^{eq}(aq)}$ approaches the vapour pressure of pure liquid water $\mathrm{p_1^*(\ell)}$ at the same temperature. At this stage we introduce the concept of an ideal solution. We assert that for an ideal solution the approximation (a) is an equation. Thus

$$\mathrm{p_1^{eq}(aq; id) = p_1^*(\ell)\, x_1}$$

In other words, $\mathrm{p_1^{eq}(aq; id)}$ is a linear function of mole fraction composition of the solution [1]. We have linked the (equilibrium) vapour pressure of the **solvent** to the composition of the **solution**. Returning to the results of experiments, we invariably find that as **real** solution becomes more dilute (*i.e.* as $\mathrm{x_1}$ approaches unity) $\mathrm{p_1^{eq}(aq)}$ for real solutions approaches $\mathrm{p_1^{eq}(aq; id)}$ for the corresponding ideal solution at the same temperature. Therefore, we rewrite equation (b) as an equation for real solutions by introducing a new quantity called the (rational) activity coefficient, $\mathrm{f_1}$. Then,

$$\mathrm{p_1^{eq}(aq) \cong p_1^*(\ell)\, x_1\, f_1}$$

where, by definition,

$$\mathrm{limit\ (x_1 \to 0)\, f_1 = 1.0}$$

Although equations (c) and (d) have simple forms, rational activity coefficients carry a heavy load in terms of information. Thus for a given solution $\mathrm{f_1}$ describes the extent to which interactions involving solvent water in the real solution differ from those in the corresponding ideal solution. The challenge of expressing this information in molecular terms is formidable.

Footnotes

[1] Note that, $\mathrm{p_1^{eq}(aq; id) - p_1^*(\ell) < 0}$. Thus adding a solute lowers the vapour pressure of the solvent. However the total vapour pressure of a binary liquid mixture can be either increased or decreased by adding a small amount of solute, the change being characteristic of the solute; G. Bertrand and C. Treiner, J. Solution Chem.,1984,**13**, 43.

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1.10.6: Gibbs Energies- Solutions- Pairwise Solute Interaction Parameters

A given solution is prepared using $1\ \mathrm{kg}$ of water(ℓ) and $\mathrm{m_j}$ moles of solute j. The chemical potential of the solvent water is related to $\mathrm{m_j}$ using equation (a) where pressure p is close to the standard pressure, $\mathrm{p^0}$

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - \phi\,\mathrm{R\,T\,m_j\,M_1}$$

Here $\mu_1^*(\ell)$ is the chemical potential of solvent water at the same T and p; ϕ is the practical osmotic coefficient which is unity for a solution having thermodynamic properties which are ideal; $\mathrm{M_1}$ is the molar mass of water. The chemical potential of the solute j, $\mu_j(\mathrm{aq})$ is related to the molality $\mathrm{m_j}$ using equation (b).

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_j\,\gamma_j/m^0\right)}$$

The chemical potentials of solute and solvent are linked by the Gibbs-Duhem equation which for aqueous solutions (at fixed T and p) containing $1\ \mathrm{kg}$ of water takes the following form.

$$(1/\mathrm{M_1})\ \mathrm{d}\mu_1(\mathrm{aq}) + \mathrm{m_j}\,\mathrm{d}\mu_\mathrm{j}(\mathrm{aq}) = 0$$

We draw equations (a) and (b) together in an equation for the Gibbs energy of a solution prepared using $1\ \mathrm{kg}$ of solvent water. Then [1],

$$\mathrm{G\,(aq;\,w_1 = 1\ kg)} = (1/\mathrm{M_1})\ \mu_1(\mathrm{aq}) + \mathrm{m_j}\,\mu_\mathrm{j}(\mathrm{aq})$$

Or,

$$\begin{aligned}\mathrm{G\,(aq;\,w_1 = 1\ kg)} = (1/\mathrm{M_1})\ &[\mu_1^*(\ell) - \phi\,\mathrm{R\,T\,m_j\,M_1}] \\ &+ \mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_j\,\gamma_j/m^0\right)}\right]\end{aligned}$$

If the thermodynamic properties of the solution are ideal, both ϕ and γ_j are unity.

$$\begin{aligned}\mathrm{G\,(aq;\,w_1 = 1\ kg;\,id)} = (1/\mathrm{M_1})\ &[\mu_1^*(\ell) - \mathrm{R\,T\,m_j\,M_1}] \\ &+ \mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_j/m^0\right)}\right]\end{aligned}$$

The difference between $\mathrm{G(aq)}$ and $\mathrm{G(aq;\,id)}$ is the excess Gibbs energy $\mathrm{G^E(aq)}$ [2];

$$\mathrm{G^E(aq) = R\,T\,m_j\ [1 - \phi + ln\,(\gamma_j)]}$$

A related quantity is the excess molar Gibbs energy \(\mathrm{G}_{\mathrm{m}}^{\mathrm{E}}(\mathrm{aq}) \quad\left\{=\mathrm{G}^{\mathrm{E}} / \mathrm{m}_{\mathrm{j}}\right\} \nonumber \]

. Then [3]

$$\mathrm{G_m^E(aq) = R\,T\ [1 - \phi + ln\,(\gamma_j)]}$$

The dependence of $\mathrm{G^E(aq)}$ on $\mathrm{m_j}$ emerges from equation (g).

$$(1/\mathrm{R\,T})\,\mathrm{d}\left[\mathrm{G^E(aq)/m_j}\right] = \mathrm{d}(1-\phi) + \mathrm{d\,ln\,(\gamma_j)}$$

But, from the Gibbs-Duhem equation,

$$\mathrm{d\,ln\,(\gamma_j)} = -\,(1/\mathrm{m_j})\ \mathrm{d\,[m_j\,(1-\phi)]}$$

Then [4]

$$(1/\mathrm{R\,T})\,\mathrm{d}\left[\mathrm{G^E(aq)/m_j}\right] = -\,[(1-\phi)/\mathrm{m_j}]\ \mathrm{dm_j}$$

Equation (k) relates $(1-\phi)$ to the dependence of $\mathrm{G^E(aq)}$ on molality $\mathrm{m_j}$. The relationship between $\mathrm{G^E(aq)}$ and γ_j is given by equation (l) [5].

$$\mathrm{ln\,(\gamma_j)} = (1/\mathrm{R\,T})\ \left[\mathrm{dG^E(aq)/dm_j}\right]$$

At this point we make a key extrathermodynamic assumption. We assert that (at fixed temperature and pressure) the excess Gibbs energy $\mathrm{G^E}$ is related to molality $\mathrm{m_j}$ of neutral solute j using equation (m). Thus

$$G^E = g_{ij}\ (m_j/m^0)^2 + g_{ij} + (m_j/m^0)^3 \ldots\ldots$$

Here $g_{jj}, g_{jjj} \ldots$ are the coefficients in a virial type of equation. Thus g_{jj} measures the contribution of pairwise solute-solute interactions to $G^E(aq)$; g_{jjj} is a triplet interaction term. For quite dilute solutions the dependence of $G^E(aq)$ on m_j is effectively described by the pairwise term, g_{jj}.

$$G^E = g_j\ (m_j/m^0)^2$$

Here g_{jj} is expressed in $[Jkg^{-1}]$, being the (Gibbs) energy of interaction in a solution containing $1\ kg$ of water. Pairwise solute-solute Gibbs energy interaction parameters are characteristic of solute j, temperature and pressure.

At this stage we have not defined either the sign or magnitude of g_{jj}. Clearly if pairwise solute-solute interactions are attractive/cohesive, both g_{jj} and G^E are negative. In the next stage of the analysis we use equation (l) to obtain an equation for $\ln(\gamma_j)$ in terms of g_{jj} and molality m_j. Thus [6]

$$\ln(\gamma_j) = [2/RT]\, g_{jj}\ (m^0)^{-2}\ m_j$$

Hence equation (o) requires that (at fixed T and p) if g_{jj} is negative $\ln(\gamma_j)$ decreases with increase in m_j whereby $\mu_j(aq) < \mu_j(aq;id)$. We anticipate that the sign and magnitude of g_{jj} reflect the hydration characteristics of the two solute molecules because these characteristics determine the impact of cosphere overlap on the properties of the solution.

We turn to the properties of the solvent. Thus [7]

$$(1-\phi) = -(1/RT)\, g_{ij}\ (m^0)^{-2}\ m_j$$

Or,

$$\phi = 1 + (1/RT)\, g_j\ (m^0)^{-2}\ m_j$$

From the equation for $[\mu_1(aq) - \mu_1(aq;id)]$, the difference in chemical potentials of solvent water in real and ideal solutions, it follows that negative g_{jj} requires that $\mu_1(aq) > \mu_1(aq;id)$, the solvent in the real solution being at a higher chemical potential than in the corresponding ideal solution. In other words the non-ideal properties of the solvent are also related to the pairwise interaction parameter g_{jj} and m_j.

As a check on the procedures described above we draw the equations together to recover the original equation for $G^E(aq)$.

$$\begin{aligned} G^E(aq) &= m_j\, RT\ [1 - \phi + \ln(\gamma_j)] \\ &= m_j\, RT\ \left[-(1/RT)\, g_{jj}\ (1/m^0)^2\ m_j + (2/RT)\, g_j\, m_j\ (1/m^0)^2\right] \\ &= g_{jj}\ (m_j/m^0)^2 \end{aligned}$$

Thus for dilute solutions both ϕ and $\ln(\gamma_j)$ are linear functions of m_j. Equation (n) forms the basis for understanding the properties of dilute aqueous solutions where the solutes are non-ionic [8]. The underlying theme is the idea that solute -solute interactions in these solutions can be understood in terms of cosphere- cosphere interactions [9,10]. Description of the properties of real solutions based on equation (a) is closely related to descriptions of dilute solutions developed for metallurgical systems [11,12]. Similarly procedures are discussed using site-site pair correlation functions for molecular interaction energies [13] and using quasi-chemical models [14].

Footnotes

[1] $G\,(aq; W_1 = 1\ kg] = [kgmol^{-1}]^{-1}\ [Jmol^{-1}] + [molkg^{-1}]\ [Jmol^{-1}] = [Jkg^{-1}]$

[2] $G^E(aq) = [JK^{-1}\ mol^{-1}]\ [K]\ [molkg^{-1}]\ [I] = [Jkg^{-1}]$

[3] $G_m{}^E(aq) = [JK^{-1}\ mol^{-1}]\ [K]\ [I] = [Jmol^{-1}]$

[4]

$$(1/\mathrm{R\,T})\,\mathrm{d}\left[\mathrm{G^E(aq)/m_j}\right] = \mathrm{d}(1-\phi) - (\mathrm{l/m_j})\;\mathrm{d}\left[\mathrm{m_j}\,(1-\phi)\right]$$
$$(1/\mathrm{R\,T})\,\mathrm{d}\left[\mathrm{G^E(aq)/m_j}\right] = \mathrm{d}(1-\phi) - \mathrm{d}(1-\phi) - \left[(1-\phi)/\mathrm{m_j}\right]\,\mathrm{dm_j}$$
$$(1/\mathrm{R\,T})\,\mathrm{d}\left[\mathrm{G^E(aq)/m_}j\right] = -\left[(1-\phi)/\mathrm{m_j}\right]\,\mathrm{dm_j}$$

[5] From equation (g), $\mathrm{G^E(aq)} = \mathrm{R\,T\,m_j}\;[1-\phi+\ell\mathrm{n}\,(\gamma_\mathrm{j})]$

$$(1/\mathrm{R\,T})\,\mathrm{dG^E(aq)/dm_j} = (1-\phi) - \mathrm{m_j}\;(\mathrm{d}\phi/\mathrm{dm_j}) + \ell\mathrm{n}\,(\gamma_\mathrm{j}) + \mathrm{m_j}\,\mathrm{d}\ell\mathrm{n}\,(\gamma_\mathrm{j})\,/\mathrm{dm_j}$$

But from the Gibbs-Duhem equation, $\mathrm{d}\left[\mathrm{m_j}.(1-\phi)\right] + \mathrm{m_j}\,\mathrm{d}\ell\mathrm{n}\,(\gamma_\mathrm{j}) = 0$

Or,

$$-\mathrm{m_j}\,\mathrm{d}\phi + (1-\phi)\,\mathrm{dm_j} + \mathrm{m_j}\,\mathrm{d}\ell\mathrm{n}\,(\gamma_j) = 0$$

Or,

$$-\mathrm{m_j}\;(\mathrm{d}\phi/\mathrm{dmm_j}) + (1-\phi) + \mathrm{m_j}\,\mathrm{d}\ell\mathrm{n}\,(\gamma_\mathrm{j})\,/\mathrm{dm_j} = 0$$

[6]

$$\ell\mathrm{n}\,(\gamma_j) = (1/\mathrm{R\,T})\,\mathrm{d}\left[\mathrm{g_{jj}}\;\left(\mathrm{m_j/m^0}\right)^2\right]/\mathrm{dm_j}$$
$$\ell\mathrm{n}\,(\gamma_\mathrm{j}) = (2/\mathrm{R\,T})\,\mathrm{g_j}\;\left(\mathrm{m^0}\right)^{-2}\;\mathrm{m_j}$$

Or, $[1] = [1]\;\left[\mathrm{Jmol^{-1}K^{-1}}\;\left[\mathrm{K^{-1}}\;\left[\mathrm{Jkg^{-1}}\right]\;\left[\mathrm{molkg^{-1}}\right]^{-2}\;\left[\mathrm{molkg^{-1}}\right]\right.\right.$

[7] From, $\mathrm{G^E(aq)} = \mathrm{R\,T\,m_j}\;[1-\phi+\ln\,(\gamma_\mathrm{j})]$ But $\mathrm{G^E(aq)} = \mathrm{g_{ij}}\;\left(\mathrm{m_j/m^0}\right)^2$

Then, $\mathrm{g_j}\;\left(\mathrm{m_j/m^0}\right)^2/\mathrm{R\,T} = \mathrm{m_j}\,(1-\phi) + (2/\mathrm{R\,T})\,\mathrm{g_j}\;\left(\mathrm{m^0}\right)^{-2}\;\left(\mathrm{m_j}\right)^2$

Then $(1-\phi) = -(1/RT)\;g_{ij}\;\left(m^0\right)^{-2}\;m_j$

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1.10.7: Gibbs Energies- Solutions- Parameters Phi and ln(gamma)

The practical osmotic coefficient can be calculated knowing the dependence of γ_j on molality of solute j. Of course at this stage we do not know the form of the dependence of γ_j on m_j. In fact γ_j also depends on the solute, temperature and pressure. But for a given system (at fixed T and p) we might express ϕ as a series expansion of the molality m_j. Thus,

$$\phi = 1 + a_1 m_j + a_2 m_j^2 + a_3 m_j^3 + \ldots\ldots$$

Interestingly this assumed dependence is equivalent to a series expansion in mole fraction of solute x_j for $\ln f_1$, where f_1 is the (rational) activity coefficient for the solvent [1,2].

$$\ln f_1 = b_1 x_j^2 + b_1 x_j^3 + b_3 x_j^4 + \ldots\ldots$$

Here $b_1,\ b_2,\ b_3 \ldots$ depend on the solute (for given T and p). The link between the two equations can be expressed as follows.

$$b_1 = -\left[(1/2) + M_1^{-1} a_1\right]$$

$$b_2 = -\left[(2/3) + 2 M_1^{-1} a_1 + M_1^{-2} a_2\right]$$

$$b_3 = -\left[(3/4) + 3 M_1^{-1} a_1 + 3 M_1^{-2} a_2 + a_3 M_1^{-3}\right]$$

Footnotes

[1] J. J. Kozak, W. S. Knight and W. Kauzmann, J. Chem. Phys., 1968,**48**, 675.

[2] By definition, for a solution j in solvent, chemical substance 1,

$$x_j = m_j / \left(M_1^{-1} + m_j\right)$$

where M_1 is the molar mass of solvent expressed in kgmol^{-1}. Hence molality of solute j,

$$m_j = x_j M_1^{-1} \left(1 - x_j\right)^{-1}$$

We expand $(1 - x_j)^{-1}$ based on the premise that $0 < x_j << 1.0$ for dilute solutions. Then,

$$m_j = x_j M_1^{-1} \left[1 + x_j + x_j^2 + x_j^3 + \ldots\ldots\right]$$

or, m x j jj jj M x x x = ·+ + ++ − 1 1 234 [.....] (d)

Here we carry all terms up to and including the fourth power of xj. But from the two methods for relating μ1(aq) to the composition of a solution, 1nx f M m 11 1 j ( ) · =−· · φ (e)

Then, 1 1 11 1 1 2 2 3 3 nx f M m m m m j jjj ( ) [.....] · =− · · + · + · + · + a a a (f)

or, 1 11 1 11 2 2 3 3 4 nf n M m m m m j jj j j x a a a =− − − · + · + · + · + ( ) [.....] (g)

But for dilute solutions, −− =+ + + 11 2 3 4 2 34 nx x x x j jj j j ( ) (/) (/) (/) x (h)

Using equation (c) for mj as a function of xj in the context of equation (f), we obtain an equation for ln(f1). 1 234 1 2 34 nf x x x jj j j ( ) (/) (/) (/) x =+ + + −− − − xxxx jj jj 234 1 4 j 1 1 1 3 j 1 1 1 2 j 1 1 − M · x · a − 2 · M · x · a − 3· M · x · a − − − − · · –· · · − − M xa M xa 1 j j 2 3 2 1 2 4 2 3 − ·· − M xa 1 j 3 4 3 (i)

Hence, 1n(f1) = { [(/) ( )] } − +· · − 1 2 1 1 1 2 a M x j } { [(2 / 3) (2 a M) (a M)] x3 j 2 2 1 1 1 1 + − + · · + · · − − +− + · · + · · + · · − −− { [/) ( ) ( ) ( )] } 34 3 3 1 1 1 2 1 2 3 1 3 4 aM aM aM x j (j)

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1.10.8: Gibbs Energies- Solutions- Solute-Solute Interactions

In real solutions, solute molecules are not infinitely far apart. With increase in solute concentration, the mean separation of solute molecules decreases [1]. Deviations in the properties of real solutions of neutral solutes from ideal can be understood in term of contact, overlap and interaction between cospheres of solvent surrounding solute molecules [2]. Two limiting cases can be identified. In one case overlap occurs between cospheres for which the organisation of solvent molecules are compatible, leading to attractive interaction between two solute molecules; a stabilising effect. In the opposite case the organisation of solvent in the cospheres is incompatible leading to repulsion between the solute molecules; i.e a destabilising effect. These ideas can be formulated quantitatively leading to an understanding of the factors controlling the properties of solutes in aqueous solution.

A given solution is prepared using $1\ \mathrm{kg}$ of water(ℓ) and m_j moles of solute j. The chemical potential of the solvent water is related to m_j using equation (a).

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - \phi\,\mathrm{R\,T\,m_j\,M_1}$$

Here $\mu_1^*(\ell)$ is the chemical potential of solvent water at the same T and p; ϕ is the practical osmotic coefficient which is unity for a solution having thermodynamic properties which are ideal; M_1 is the molar mass of water. The difference $[\mu_1(\mathrm{aq}) - \mu_1^*(\ell)]$ equals $[-\phi\,\mathrm{R\,T\,m_j\,M_1}]$. Hence for an ideal solution where ϕ is unity addition of a solute lowers the chemical potential of the solvent; i.e. stabilises the solvent.

The chemical potential of the solute $\mu_\mathrm{j}(\mathrm{aq})$ is related to the molality m_j using equation (b).

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)$$

We rewrite equation (b) in an extended form.

$$\mu_j(aq) = \mu_j^0(aq) + RT\,\ln\left(m_j/m^0\right) + RT\,\ln\left(\gamma_j\right)$$

Or,

$$\mu_\mathrm{j}(\mathrm{aq;id}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}/\mathrm{m}^0\right)$$

Hence γ_j measures the extent to which the chemical potential of solute j in the real solution differs from that in an ideal solution. If $\gamma_j > 1$ [and hence $\ln(\gamma_j) > 0$] $\mu_j(\mathrm{aq}) < \mu_\mathrm{j}(\mathrm{aq;id})$, solute-solute interactions destabilise the solute. If $\gamma_\mathrm{j} < 1$ [and hence $\ln(\gamma_\mathrm{j}) < 0$] $\mu_\mathrm{j}(\mathrm{aq}) > \mu_\mathrm{j}(\mathrm{aq;id})$, and so these interaction stabilise the solute. [NBγ_j cannot be negative.]

The chemical potentials of solute and solvent are linked by the Gibbs – Duhem equation which for aqueous solutions (at fixed T and p) containing $1\ \mathrm{kg}$ of water takes the following form.

$$(1/M_1)\ d\mu_1(aq) + m_j\,d\mu_j(aq) = 0$$

Then,

$$(1/\mathrm{M_1})\ \mathrm{d}\left[\mu_1^*(\ell) - \phi\,\mathrm{R\,T\,m_j\,M_1}\right] + \mathrm{m_j\,d}\left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)\right] = 0$$

Or,

$$-\mathrm{d}\left[\phi\,\mathrm{m_j}\right] + \mathrm{m_j\,d\,ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right) = 0$$

The latter equation links changes in the osmotic coefficient ϕ and γ_j. In other words, a perturbation which affects the solvent feeds back on to the properties the solute. This is Gibbs-Duhem communication. In the present context equation (g) explains why interaction between cospheres feeds back to the properties of the solute. Consequently the Gibbs-Duhem equation is used to switch between equations describing ϕ and γ_j. Thus from equation (g),[3]

$$\mathrm{d}\left[\mathrm{m_j}\,(1-\phi)\right] + \mathrm{m_j\,d\,ln}\left(\gamma_\mathrm{j}\right) = 0$$

Equation (h) can be written in two forms depending which direction we wish to proceed. Thus from equation (h)[4],

$$(1-\phi) = -(1/m_j)\int_{m(j)=0}^{m(j)} m_j\, d\ln(\gamma_j)$$

In other words we have an equation for ϕ and in terms of γ_j. Alternatively [5] we can express γ_j in terms of ϕ and its dependence on m_j.

$$\int_{m(j)=0}^{m(j)} d\ln(\gamma_j) = \int_{m(j)=0}^{m(j)} d(1-\phi) + \int \left[(1-\phi)/m_j\right] dm_j$$

Then

$$\ln(\gamma_j) = (\phi - 1) + \int_{\mathrm{m(j)}=0}^{\mathrm{m(j)}} (\phi-1)\,\mathrm{d}\ln(\mathrm{m_j})$$

Hence γ_j can be calculated from knowing ϕ and its dependence on dependence on m_j.

Footnotes

[1] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd. edn.,1959, chapter 1.

[2] J. J. Kozak, W. S. Knight and W. Kauzmann, J. Chem. Physics,1968,**48**,675.

[3] $-\phi\, dm_j - m_j\, d\phi + m_j\, dm_j/m_j + m_j\, \ln(\gamma_j) = 0$
Or, $\mathrm{dm_j} - \phi\, d\ \mathrm{m_j} - \mathrm{m_j}\,\mathrm{d}\phi + \mathrm{m_j}\ \ln(\gamma_j) = 0$

[4] $\int_{\mathrm{m(j}j=0}^{\mathrm{m(j)}} \mathrm{d}\left[\mathrm{m_j}\,(1-\phi)\right] = -\int_{\mathrm{m(j)}=0}^{\mathrm{m(j)}} \mathrm{m_j}\,\mathrm{d}\ln(\gamma_j)$
$\mathrm{m_j}\,(1-\phi) = -\int_{\mathrm{m(j)}=0}^{\mathrm{m(j)}} \mathrm{m_j}\,\mathrm{d}\ln(\gamma_j)$

[5] From equation (h), $\mathrm{d}\ln(\gamma_j) = (1/\mathrm{m_j})\ \mathrm{d}\left[\mathrm{m_j}\,(\phi-1)\right]$

Or,

$$\int_{m(j)=0}^{m(j)} d\ln(\gamma_j) = \int_{m(j)=0}^{m(j)} d(\phi-1) + \int \left[(\phi-1)/m_j\right] dm_j$$

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1.10.9: Gibbs Energies- Solutes- Cospheres

The chemical potential of solute j in aqueous solution, molality m_j, at temperature T and pressure p (which is close to ambient) is given by equation (a).

$$\mu_{\mathrm{j}}(\mathrm{aq}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right)$$

In developing an understanding the of factors which contribute to $\mu_{\mathrm{j}}(\mathrm{aq})$, a model for solutions developed by Gurney is often helpful [1].

A co-sphere is identified around each solute molecule j where the organization of solvent molecules differs from that in the bulk solvent at the same T and p. In a solution where the thermodynamic properties of the solute j are ideal, there are no solute-solute interactions such that the activity coefficient γ_j is unity. In real solutions the fact that $\gamma_j \neq 1$ can be understood in terms of co-sphere---co-sphere interactions together for salt solutions strong charge-charge interactions.

The model [2] identifies two zones. Zone A describes solvent molecules close to the solute molecule, the number of such solvent molecules being the primary hydration number. Zone B describes the solvent molecules outside Zone A. Their organization differs from that in the bulk solvent as a consequence of the presence of solute molecule (or, ion) j. Zone C lies beyond zone B where the organization of solvent is effectively the same as that in pure solvent at the same T and p. There is merit in not being too pedantic concerning the definitions of zones A, B and C.

For real solutions co-sphere----co-sphere interactions are accounted for using for example the term $\left[\partial \ln\left(\gamma_{\mathrm{j}}\right)/\partial \mathrm{p}\right]_{\mathrm{T}}$ in the equation describing the partial molar volume $\mathrm{V_j(aq)}$ for solute j in a real solution.

Footnotes

[1] R. W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.

[2] H. S. Frank and W.-Y. Wen, Discuss. Faraday Trans.,1957,**24**,756.

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1.10.10: Gibbs Energies- Solutions- Cosphere-Cosphere Interactions

For neutral solutes in aqueous solutions, the solvent plays a key role in determining the form and magnitude of solute-solute interactions. One description of these interactions uses the Gurney model for solute cospheres.[1] Cosphere-cosphere interaction, involving the solvent, feeds back to the properties of the solute; i.e. Gibbs - Duhem communication. Two limiting cases are identified.

i. The hydration characteristics (i.e. solute-solvent interaction) of the two solute molecules, α and β are quite different such that in the region of overlap their structural influence on water-water interactions are incompatible/antagonistic. Thus the pairwise Gibbs energy interaction parameter g_{jj} is positive; $\gamma_j > 1$ and $\ln(\gamma_j) > 0$. The intuitive idea is that incompatability is synonymous with repulsion (almost human behaviour-- a dangerous anthropomorphic argument).
ii. In the second case, the hydration cospheres of the two solute molecules α and β are similar to the extent that in the region of cosphere overlap there is an enhancement of water-water interactions and hence attraction. Thus the pairwise Gibbs energy interaction parameter g_{jj} is negative; $\gamma_j < 1$ and $\ln(\gamma_j) < 0$. Where solute molecules α and β are apolar this attraction is called hydrophobic bonding/attraction.

Footnotes

[1] See for example, R. P. Currier and J. P. O'Connell, Fluid Phase Equilibria,1987,**33**,245.

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1.10.11: Gibbs Energies- Solutions- Solute-Solute Interactions- Pairwise

Analysis of the thermodynamic properties of aqueous solutions was taken a step further by Savage and Wood who envisage two solute molecules A and B in aqueous solution [1]. The total pairwise interaction between these molecules is described in terms of pairwise group-group interaction parameters. Then, for example, the pairwise enthalpic solute-solute interaction parameter \(\mathrm{H}_{\mathrm{AB}}\) is written as the sum of products, $n_i^A\ n_j^B\ h_{ij}$ where n_i^A is the number of A-groups in solute molecule i and n_j^B is the number of B-groups in solute molecule j where h_{ij} is a pairwise enthalpic group interaction parameter. A similar analysis is carried out for interaction Gibbs energies leading to pairwise Gibbs energy parameters g_{ij}. So, for example, $g(OH-OH)$ is negative characteristic of a hydrophilic-hydrophilic interaction. Whereas $g\,(OH-CH_2)$ is positive indicating 'repulsion' within hydrophobic-hydrophilic pairs. Interestingly $g\,(CH_2-CH_2)$ is negative" which is indicative of a hydrophobic-hydrophobic attraction (cf. hydrophobic bonding); the corresponding enthalpic pairwise parameter is positive. Thus it is tempting to speculate that hydrophobic attraction is entropy driven [2]; for further comments see references [3-13].

The general approach is readily extended to a consideration of pairwise interactions between added solutes and both initial and transitions states for given chemical reactions in aqueous solution [14-18].

Footnotes

[1] J.J. Savage and R. H. Wood, J. Solution Chem.,1976,**5**,733.

[2] J.J. Spitzer, S. K. Suri and R. H. Wood, J. Solution Chem.,1985,**14**,5; and references therein.

[3] S. K. Suri and R. H. Wood, J. Solution Chem.,1986,**15**,705.

[4] S. K. Suri, J.J.Spitzer, R. H. Wood, E.G.Abel and P.T. Thompson, J. Solution Chem.,1986,**14**,781.

[5] A. L. Harris, P. T. Thompson and R. H. Wood, J. Solution Chem.,1980, **9**,305.

[6] For the role of solute stereochemistry see F. Franks and M. D. Pedley, J. Chem. Soc. Faraday Trans. 1, 1983,**79**,2249.

[7] Amides in N,N-dimethvl formamide: M. Bloemendal and G. Somsen, J. Solution Chem.,1983,**12**,83.

[8] Solutions in DMF with a modification of the role of the solvent; M. Bloemendal and G. Somsen, J. Solution Chem.,1987,**16**,367

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[10]

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b. Amino acids and peptides; T H. Lilley and R. P. Scott, J. Chem. Soc. Faraday Trans. 1, 1976,**72**,359.
c. Monosaccharides(aq); G. Barone, G. Castronuovo, D. Doucas, V.Elia and G. A. Mattia, J.Phys.Chem.,1983,**87**,1931.

[11] Urea and polyols(aq); G. Barone, V. Elia and E. Rizzo, J. Solution Chem.,1982,**11**,687.

[12] Volumes and heat capacities of aromatic solutes(aq); S. Cabani, P. Gianni,V. Mollica and L. Lepori, J. Solution Chem., 1981,**10**,563.

[13] Small peptides(aq); enthalpies; O. V. Kulikov, A. Zielenkiewicz, W. Zielenkiewicz. V. G. Badelin and A.Krestov , J. Solution Chem., 1993,**22**,59.

[14] M. J. Blandamer, J. Burgess, I . M. Horn, J. B. F. N. Engberts and P. Warrick Jr., Colloids and Surfaces, 1990,**48**,139.

[15] M. J. Blandamer, J. Burgess, J. B. F. N. Engberts and W. Blokzijl, Annu. Rep. Prog. Chem., Sect C, Phys. Chem.,1990,**87**,45.

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[17] M. J. Blandamer, J. Burgess and J. B. F. N. Engberts, Chem. Soc Rev.,1985,**14**,237.

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1.10.12: Gibbs Energies- Solutions- Two Neutral Solutes

A given aqueous solution containing two neutral solutes, i and j, (e.g. urea and sucrose) was prepared using $1\ \mathrm{kg}$ of water at temperature T and pressure p (which was close to ambient). The molalities of the two solutes were $\mathrm{m_i}$ and $\mathrm{m_j}$ The chemical potential of the solvent in the mixed aqueous solution is given by equation (a) where for an ideal solution the practical osmotic coefficient ϕ is unity. Then,

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - \phi\,\mathrm{R\,T\,M_1}\ (\mathrm{m_i} + \mathrm{m_j})$$

The chemical potentials of the two solutes are related to their molalities using equations (b) and (d).

$$\mu_\mathrm{i}(\mathrm{aq}) = \mu_\mathrm{i}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_i}\,\gamma_\mathrm{i}/\mathrm{m}^0\right)$$

where

$$\mathrm{limit}\,(\mathrm{m_i} \to 0; \mathrm{m_j} \to 0)\,\gamma_\mathrm{i} = 1.0 \quad (\mathrm{at\ all\ T\ and\ p})$$

Similarly,

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)$$

where

$$\mathrm{limit}\,(\mathrm{m_i} \to 0; \mathrm{m_j} \to 0)\,\gamma_\mathrm{j} = 1.0 \quad (\mathrm{at\ all\ T\ and\ p})$$

Therefore the Gibbs energy of a solution prepared using $1\ \mathrm{kg}$ of water is given by equation (f).

$$\begin{aligned}\mathrm{G}\,(\mathrm{aq}; \mathrm{w_1/kg} = 1.0) = (1/\mathrm{M_1})\,[\mu_1^*(\ell) - \phi\,\mathrm{R\,T\,M_1}\ (\mathrm{m_i} + \mathrm{m_j})] \\ +\mathrm{m_i}\ \left[\mu_\mathrm{i}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_i}\,\gamma_\mathrm{i}/\mathrm{m}^0\right)\right] \\ +\mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)\right]\end{aligned}$$

For the corresponding solution having ideal thermodynamic properties

$$\begin{aligned}\mathrm{G}\,(\mathrm{aq}; \mathrm{w_1/kg} = 1.0) = (1/\mathrm{M_1})\ [\mu_1^*(\ell) - \mathrm{R\,T\,M_1}\ (\mathrm{m_i} + \mathrm{m_j})] \\ +\mathrm{m_i}\ \left[\mu_\mathrm{i}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_i}/\mathrm{m}^0\right)\right] \\ +\mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}/\mathrm{m}^0\right)\right]\end{aligned}$$

But the excess Gibbs energy is defined by equation (h).

$$\mathrm{G^E(aq)} = \mathrm{G(aq)} - \mathrm{G(aq; id)}$$

Hence

$$\mathrm{G^E(aq)/R\,T} = (\mathrm{m_i} + \mathrm{m_j})\ (1 - \phi) + \mathrm{m_j\ ln}\,(\gamma_\mathrm{j}) + \mathrm{m_i\ ln}\,(\gamma_\mathrm{i})$$

Actually ϕ, γ_i and γ_j are linked. They cannot change independently. According to the Gibbs-Duhem equation (at fixed T and p),

$$(1/M_1)\ d\mu_1(aq) + m_j\,d\mu_j + m_i\,d\mu_i = 0$$

We consider the case where the solution is perturbed by a change in molality, $\mathrm{dm_j}$, recognising that the chemical potentials of solvent and solutes change. Thus,

$$(1/M_1)\ (d\mu_1(aq)/dm_j) + m_j\ (d\mu_j/dm_j) + m_i\ (d\mu_i/dm_j) = 0$$

Therefore from equation (j),

$$\begin{aligned}(1/\mathrm{M_1})\ \frac{\mathrm{d}}{\mathrm{dm_j}}\ [\mu_1^*(\ell) - \phi\,\mathrm{R\,T\,M_1}\ (\mathrm{m_i} + \mathrm{m_j})] \\ +\mathrm{m_i}\,\frac{\mathrm{d}}{\mathrm{dm_j}}\ \left[\mu_\mathrm{i}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_i}\,\gamma_\mathrm{i}/\mathrm{m}^0\right)\right] \\ +\mathrm{m_j}\,\frac{\mathrm{d}}{\mathrm{dm_j}}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)\right] = 0\end{aligned}$$

In the case considered here molality $\mathrm{m_i}$ does not change. Then (at constant, $\mathrm{m_i}$, T, p and mass of solvent),

$$-\left(\mathrm{m_i}+\mathrm{m_j}\right)\left[\frac{\partial\phi}{\partial \mathrm{m_j}}\right]_{\mathrm{m(i)}}+(1-\phi)+\mathrm{m_j}\left[\frac{\partial \ln\left(\gamma_\mathrm{j}\right)}{\partial \mathrm{m_j}}\right]_{\mathrm{m(i)}}+\mathrm{m_i}\left[\frac{\partial \ln\left(\gamma_\mathrm{i}\right)}{\partial \mathrm{m_j}}\right]_{\mathrm{m(i)}}=0$$

With the help of the latter equation we explore how the Gibbs energy depends on the molality of solute j at constant $\mathrm{m_i}$. Then from equation (i),

$$\frac{1}{RT}\left[\frac{\partial G^{\mathrm{E}}(\mathrm{aq})}{\partial \mathrm{m_j}}\right]=-\left(\mathrm{m_i}+\mathrm{m_j}\right)\left[\frac{\partial\phi}{\partial \mathrm{m_j}}\right]_{\mathrm{m(i)}}+(1-\phi)+\mathrm{m_j}\left[\frac{\partial \ln\left(\gamma_\mathrm{j}\right)}{\partial \mathrm{m_j}}\right]_{\mathrm{m(i)}}+\ln\left(\gamma_\mathrm{j}\right)+\mathrm{m_i}\left[\frac{\partial \ln\left(\gamma_\mathrm{i}\right)}{\partial \mathrm{m_j}}\right]_{\mathrm{m(i)}}$$

Comparison of equations (m) and (n) shows that the differential dependence of $\mathrm{G^E(aq)}$ on $\mathrm{m_j}$ at constant $\mathrm{m_i}$ is related to $\ln\left(\gamma_\mathrm{s}\right)$;

$$\ln\left(\gamma_\mathrm{j}\right)=\frac{1}{\mathrm{R\,T}}\left[\frac{\partial \mathrm{G^E(aq)}}{\partial \mathrm{m_j}}\right]$$

If the solution is dilute then $\mathrm{G^E(aq)}$ can be described using pairwise Gibbs energy interaction parameters. Thus

$$\mathrm{G^E(aq)}=\mathrm{g_{ji}}\left(\mathrm{m_j}/\mathrm{m^0}\right)^2+2\,\mathrm{g_{ij}}\,\mathrm{m_i}\,\mathrm{m_j}\left(\mathrm{m^0}\right)^{-2}+\mathrm{g_{ii}}\left(\mathrm{m_i}/\mathrm{m^0}\right)^2$$

Here g_{ii} and g_{jj} are homotactic pairwise Gibbs energy interaction parameters whereas g_{ij} is the corresponding heterotactic parameter. According to equation (p) the differential dependence of $\mathrm{G^E(aq)}$ on molality $\mathrm{m_j}$ at constant $\mathrm{m_i}$ is given by equation (q). Thus,

$$\left[\frac{\partial \mathrm{G^E(aq)}}{\partial \mathrm{m_j}}\right]_{\mathrm{m(i)}}=2\,\mathrm{g_j}\left(\mathrm{m^0}\right)^{-2}\mathrm{m_j}+2\,\mathrm{g_{ij}}\left(\mathrm{m^0}\right)^{-2}\mathrm{m_i}$$

Combination of equations (o) and (q) yields an equation for $\ln\left(\gamma_j\right)$ as a function of two pairwise interaction parameters. Then [1],

$$\ln\left(\gamma_\mathrm{j}\right)=\left[\frac{2}{RT}\right]\left[\frac{1}{m^0}\right]^2\left[g_{ij}\,m_j+g_{ij}\,m_i\right]$$

In other words $\ln\left(\gamma_\mathrm{j}\right)$ is simply related to the molality of the two solutes. In many applications we are concerned with a solution in which $\mathrm{m_i} >> \mathrm{m_j}$ such that the solution contains only a trace of solute j. The activity coefficient for solute j is written $\gamma_\mathrm{j}^\mathrm{T}$. The latter describes the effect of solute-solute interactions on solute j. If we set $\mathrm{m_j}\cong 0$, then equation (r) yields an equation for $\gamma_\mathrm{j}^\mathrm{T}$ in terms of $\mathrm{m_i}$.

$$\ln\left(\gamma_\mathrm{j}^\mathrm{T}\right)=\left[\frac{2}{\mathrm{R\,T}}\right]\left[\frac{1}{\mathrm{m^0}}\right]^2\mathrm{g_{ij}}\,\mathrm{m_i}$$

Footnote

[1] $\ln\left(\gamma_\mathrm{j}\right)=\left[\frac{2}{[\,\mathrm{J\ K^{-1}\ mol^{-1}}]\,[\mathrm{K}]}\right]\left[\frac{1}{[\,\mathrm{mol\ kg^{-1}}]}\right]^2\left[\mathrm{Jkg^{-1}}\right]\left[\mathrm{molkg^{-1}}\right]$

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1.10.13: Gibbs Energies- Solutions- Hydrates in Aqueous Solution

An explanation of the properties of a given solute j in aqueous solutions is in terms of the formation of a hydrate; j.hJH_2O where h is the hydration number independent of temperature and pressure[1]. In summary there are two descriptions of the solutions prepared using $\mathrm{n_1}$ moles of water and n_j moles of solute j. In description A there are n_j moles of solute, chemical substance j, and n1 moles of solvent. In description B there are nj moles of solute j.hH_2O and $(n_1 - h\,n_j)$ moles of water [2]. At fixed T and p the system is at equilibrium, being therefore at a minimum in Gibbs energy. The Gibbs energy is not dependent on our description of the system [3]; it does not know which description we favour!

We imagine two open dishes in a partially evacuated chamber at constant T. Each dish contains the same amount of a given solution but we label one dish A and the other dish B [4]. Further the Gibbs energies are equal; $\mathrm{G(A) = G(B)}$. The vapour pressures are the same so that $\mu_1(\mathrm{aq;A}) = \mu_1(\mathrm{aq;B})$. For dish A,

$$\mathrm{G(A) = n_1\,\mu_1(aq) + n_j\,\mu_j(aq)}$$

For dish B.

$$\mathrm{G(B) = (n_1 - n_j\,h)\;\mu_1(aq) + n_{jh}\,\mu_{jh}(aq)}$$

Here $\mu_{j\,\mathrm{h}}(\mathrm{aq})$ is the chemical potential of hydrate j.hH_2O in solution. We notes that $\mathrm{n_j = n_{jh}}$. Because $\mathrm{G(A) = G(B)}$, and the chemical potentials of the solvent are the same, $\mu_{jh}(aq) = \mu_j(aq) + h\;\mu_1(aq)$. The molality of hydrate j.hH_2O, $\mathrm{m_{jh}}$ $= \mathrm{n_{jh}/\left[(n_1 - h\,n_{jh})\;M_1\right]}$ whereas the molality of solute j $\mathrm{m_j = n_j/\left[n_1\,M_1\right]}$. Then at fixed T and p,

$$\mu^0_{\mathrm{jh}}(\mathrm{aq}) + \mathrm{R\,T\,ln\left(m_{jh}\,\gamma_{jh}/m^0\right)} =$$
$$\mu^0_{\mathrm{j}}(\mathrm{aq}) + \mathrm{R\,T\;ln\left(m_j\,\gamma_j/m^0\right) + h\;\{}\mu^*_1(\ell) - \phi\,\mathrm{R\,T\,M_1\,m_j\}}$$

In the $\mathrm{limit\,(m_j \to 0)\,\gamma_j = 1.0}$ at all T and p; in the $\mathrm{limit\,(m_{jh} \to 0)\,\gamma_{jh} = 1.0}$ at all T and p. In the same limit, $\phi = 1$. Hence assuming h is independent of m_j.

$$\mu^0_{\mathrm{jh}}(\mathrm{aq}) = \mu^0_{\mathrm{j}}(\mathrm{aq}) + \mathrm{h}\,\mu^*_1(\ell)$$

We use equation (d) and reorganise equation (c) as an equation for γ_j.

$$\mathrm{ln\,(\gamma_j) = ln\,(m_{jh}/m_j) + h\,\phi\,M_1\,m_j + ln\,(\gamma_{jh})}$$

We assert that the formation of hydrate by solute j accounts for the fact that the properties of solute j are not ideal. We also assert that the properties of the hydrate are ideal; $\gamma_{\mathrm{jh}} = 1$. Moreover, $\mathrm{(m_j/m_{jh}) = 1 - (h\,m_j\,M_1)}$ Then,

$$\mathrm{ln\,(\gamma_j) = -\,ln\,[1 - (h\,m_j\,M_j)] + h\,\phi\,M_1\,m_j}$$

If the solution is dilute , $\phi \cong 1$. Then,

$$\mathrm{ln\,(\gamma_j) = 2\,h\,m_j\,M_1}$$

The hydrate model for activity coefficients can be understood in the following fashion. When δn_j moles of solute are added to a solution molality m_j, $\mathrm{h\;\delta n_j}$ moles of water are removed from 'solvent' and transferred to the solute. In these terms each solute molecule responds to this increased competition for solvent by other solute molecules and therefore 'knows' that there are other solute molecules in the solution. Any communication between solute molecules in solution is reflected in the extent to which γ_j differs from unity.

Footnotes

[1] L. P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, 2nd. Edn., 1970,Section 2.13.

[2] $\mathrm{h\,n_j}$ must be $< \mathrm{n_1}$

[3] E. Grunwald, Thermodynamics of Molecular Species, Wiley, New York, 1977, chapter 2.

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1.10.14: Gibbs Energies- Salt Hydrates

An aqueous solution is prepared using $mathrmn_{\mathrm{j}}$ moles of salt MX and n_1 moles of water. The properties of the system are accounted for using one of two possible Descriptions.

Description I

The solute j comprises a 1:1 salt MX molality $\mathrm{m(MX)}\,[=\mathrm{n(MX)/w}_1$ where w_1 is the mass of water]. The single ion chemical potentials, are defined in the following manner

$$\mu\left(\mathrm{M}^{+}\right)=\left[\partial \mathrm{G} / \partial \mathrm{n}\left(\mathrm{M}^{+}\right)\right]_{\mathrm{T,p,n}_1,\mathrm{n}\left(\mathrm{x}^{-}\right)}$$
$$\mu\left(\mathrm{X}^{-}\right)=\left[\partial \mathrm{G} / \partial \mathrm{n}\left(\mathrm{X}^{-}\right)\right]_{\mathrm{T,p,n}_1,\mathrm{n}\left(\mathrm{M}^{+}\right)}$$

Then the total Gibbs energy (at fixed T and p) is given by equation (b). $\mathrm{G(aq;I)}=\mathrm{n}_1\,\mu_1\mathrm{(aq)}$

$$+\mathrm{n_j}\left\{\mu^{\#}\left(\mathrm{M}^{+};\mathrm{aq}\right)+\mathrm{R\,T}\,\ln\left[\mathrm{m}\left(\mathrm{M}^{+}\right)\,\gamma_{+}\mathrm{(I)/m}^{0}\right]\right\}$$
$$+\mathrm{n_j}\left\{\mu^{\#}\left(\mathrm{X}^{-};\mathrm{aq}\right)+\mathrm{R\,T}\,\ln\left[\mathrm{m}\left(\mathrm{X}^{-}\right)\,\gamma_{-}\mathrm{(I)/m}^{0}\right]\right\}$$

Description II

According to this Description each mole of cation is hydrated by $\mathrm{h_m\,(H_2O)}$ moles of water and each mole of anion is hydrated by $\mathrm{h_x\,(H_2O)}$ moles of water. Hence the single ion chemical potentials are defined as follows.

$$\mu\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O}\right)=\left[\partial \mathrm{G} / \partial \mathrm{n}\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O}\right)\right]$$

at constant T, p, $\mathrm{n}\left(\mathrm{X}^{-}\,\mathrm{h_xH_2O}\right),\left[\mathrm{n}_1-\mathrm{n_j}\,\left(\mathrm{h_m}+\mathrm{h_x}\right)\right]\mathrm{(H_2O)}$ and,

$$\mathrm{m}\left(\mathrm{X}^{-}\,\mathrm{h_xH_2O}\right)=\mathrm{n_j/M}_1\,\left[\mathrm{n}_1-\left(\mathrm{h_m}+\mathrm{h_x}\right)\,\mathrm{n_j}\right]$$

at constant T, p, $\mathrm{n}\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O}\right),\left[\mathrm{n}_1-\mathrm{n_j}\,\left(\mathrm{h_m}+\mathrm{h_x}\right)\right]\mathrm{(H_2O)}$ Then,

$$\mathrm{m}\left(\mathrm{X}^{-}\,\mathrm{h_xH_2O}\right)=\mathrm{n_j/M}_1\,\left[\mathrm{n}_1-\left(\mathrm{h_m}+\mathrm{h_x}\right)\,\mathrm{n_j}\right]$$

$$\mathrm{m}\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O}\right)=\mathrm{n_j/M}_1\,\left[\mathrm{n}_1-\left(\mathrm{h_m}+\mathrm{h_x}\right)\,\mathrm{n_j}\right]$$

Hence the (equilibrium) Gibbs energy (at defined T and p) is given by the following equation.

$$\begin{aligned}&\mathrm{G(aq)}=\left[\mathrm{n}_1-\mathrm{n_j}\,\left(\mathrm{h_m}+\mathrm{h_x}\right)\right]\,\mu_1\mathrm{(aq)}\\&\quad+\mathrm{n_j}\,\left[\mu''\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O}\right)+\mathrm{R\,T}\,\ln\left\{\mathrm{m}\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O}\right)\,\gamma_{+}\mathrm{(II)/m}^{0}\right\}\right]\\&+\mathrm{n_j}\,\left[\mu^{\mathrm{y}}\left(\mathrm{X}^{-}\,\mathrm{h_xH_2O}\right)\right.\\&\quad\left.+\mathrm{R\,T}\,\ln\left\{\mathrm{m}\left(\mathrm{X}^{-}\,\mathrm{h_xH_2O}\right)\,\gamma_{-}\mathrm{(II)}\,/\mathrm{m}^{0}\right\}\right]\end{aligned}$$

But the Gibbs energies defined by equations (b) and (g) are identical (at equilibrium at defined T and p). Hence [1],

$$\begin{aligned}&\mu''\left(\mathrm{M}^{+};\mathrm{aq}\right)+\mu''\left(\mathrm{X}^{-};\mathrm{aq}\right)+2\,\mathrm{R\,T}\,\ln\left[1-\mathrm{M}_1\,\mathrm{m_j}\,\left(\mathrm{h_m}+\mathrm{h_X}\right)\right]\\&+\mathrm{R\,T}\,\ln\left\{\gamma_{+}\mathrm{(I)}\,\gamma_{-}\mathrm{(I)}\right\}\\&=-\left(h_m+h_X\right)\,\left\{\mu_1^{*}(\ell)-2\,\phi\,R\,T\,M_1\,m_j\right\}\\&+\mu''\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O};\mathrm{aq}\right)+\mu''\left(\mathrm{X}^{-}\,\mathrm{h_XH_2O};\mathrm{aq}\right)\\&+\mathrm{R\,T}\,\ln\left\{\gamma_{+}\mathrm{(II)}\,\,\gamma_{-}\mathrm{(II)}\,\right\}\end{aligned}$$

We use the latter equation to explore what happens in the limit that n_j approaches zero. Thus, $\mathrm{limit}\,\left(\mathrm{n_j}\rightarrow 0\right)\gamma_{+}\mathrm{(I)}\,=1;\gamma_{-}\mathrm{(I)}\,=1;\gamma_{+}\mathrm{(II)}=1;\gamma_{-}\mathrm{(II)}=1;\mathrm{m_j}=0$ Hence,

$$\begin{aligned}&\mu^{\#}\left(\mathrm{M}^{+};\mathrm{aq}\right)+\mu^{\#}\left(\mathrm{X}^{-};\mathrm{aq}\right)=\\&\mu^{\#}\left(\mathrm{M}^{+}\,\mathrm{h_mH_2O};\mathrm{aq}\right)+\mu^{\#}\left(\mathrm{X}^{-}\,\mathrm{h_xH_2O};\mathrm{aq}\right)\\&-\left(\mathrm{h_m}+\mathrm{h_x}\right)\,{\mu_1}^{*}(\ell)\end{aligned}$$

We obtain an equation linking the ionic chemical potentials. Thus,

$$\ln \gamma_+(\mathrm{I}) + \ln \gamma_-(\mathrm{I}) = 2\,\phi\,\mathrm{M_1\,m_j}\,(\mathrm{h_m + h_x}) \\ -2\,\ln\left[1 - \mathrm{M_1\,m_j}\,(\mathrm{h_m + h_X})\right] \\ +\ln_+ \gamma_+(\mathrm{II}) + \ln \gamma_-(\mathrm{II})$$

Then in dilute solutions,

$$\ln \gamma_+(\mathrm{I}) + \ln \gamma_-(\mathrm{I}) = 2\,(\phi + 1)\,\mathrm{M_1\,m_j}\,(\mathrm{h_m + h_x}) \\ +\ln \gamma_+(\mathrm{II}) + \ln \gamma_-(\mathrm{II})$$

But $\ln \gamma_+(\mathrm{I}) + \ln \gamma_-(\mathrm{I}) = 2\,\ln \gamma_\pm(\mathrm{I})$ Then, $2\,\ln \gamma_\pm(\mathrm{I}) = 2\,(\phi + 1)\,\mathrm{M_1\,m_j}\,(\mathrm{h_m + h_x}) + 2\,\ln \gamma_\pm(\mathrm{II})$

We identify relationships between single ion activity coefficients in an extra-thermodynamic analysis. Thus from equation (k),

$$\ln \gamma_+(\mathrm{II}) = \ln \gamma_+(\mathrm{I}) - 2\,(\phi + 1)\,\mathrm{M_1\,m_j\,h_m}$$

$$\ln \gamma_-(\mathrm{II}) = \ln \gamma_-(\mathrm{I}) - 2\,(\phi + 1)\,\mathrm{M_1\,m_j\,h_x}$$

It is noteworthy that in these terms the solution can be ideal using description I where $\gamma_\pm = 1.0$ but non-ideal using description II. Nevertheless, these equations show how the activity coefficient of the hydrated ion (description II) is related to the activity coefficient of the simple ion (description I).

Footnote

[1] From equations (b) and (g), (dividing by n_j)

$$\left[\mu^n\,(\mathrm{M^+;aq}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{M^+;I})\;\gamma_+(\mathrm{I})/\mathrm{m^0}\right\}\right] \\ + \left[\mu''\,(\mathrm{X^-;aq}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{X^-;I})\;\gamma_-(\mathrm{I})/\mathrm{m^0}\right\}\right] = \\ -\,(h_m + h_x)\;\mu_1(aq) + \\ + \left[\mu''\,(\mathrm{M^+\,h_mH_2O;aq}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{M^+\,h_mH_2O})\;\gamma_+(\mathrm{II})\;/\mathrm{m^0}\right\}\right] \\ + \left[\mu''\,(\mathrm{X^-\,h_xH_2O}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{X^-\,h_xH_2O})\;\gamma_-(\mathrm{II})/\mathrm{m^0}\right\}\right]$$

Then

$$\mathrm{en}\;\left[\mu^*\,(\mathrm{M^+;aq}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{M^+;I})\;\gamma_+(\mathrm{I})/\mathrm{m^0}\right\}\right] \\ + \left[\mu^*\,(\mathrm{X^-;aq}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{X^-;I})\;\gamma_-(\mathrm{I})/\mathrm{m^0}\right\}\right] = \\ -\,(\mathrm{h_m + h_X})\;\{\mu_1^*(\ell) - 2\,\phi\,\mathrm{R\,T\,M_1\,m_j}\} \\ + \left[\mu^*\,(\mathrm{M^+\,h_mH_2O;aq}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{M^+\,h_mH_2O})\;\gamma_+(\mathrm{II})/\mathrm{m^0}\right\}\right] \\ + \left[\mu''\,(\mathrm{X^-\,h_xH_2O}) + \mathrm{R\,T\,ln}\left\{\mathrm{m}\,(\mathrm{X^-\,h_xH_2O})\;\gamma_-(\mathrm{II})/\mathrm{m^0}\right\}\right]$$

Or,

$$\left[\mu''\,(\mathrm{M^+;aq}) + \mu^{\#}\,(\mathrm{X^-;aq})\right. \\ \left. + \mathrm{R\,T\,ln}\left\{\mathrm{m(M^+;I)\,m}\,(\mathrm{X^-;(I)/}\,(\mathrm{M^+;II})\;\mathrm{m}\,(\mathrm{X^-;II}\right\}\right. \\ \mathrm{R\,T\,ln}\left\{\gamma_+(\mathrm{I})\,\gamma_-(\mathrm{I})\right\} \\ = -\,(\mathrm{h_m + h_X})\;\{\mu_1^*(\ell) - 2\,\phi\,\mathrm{R\,T\,M_1\,m_j}\} \\ + \mu^*\,(\mathrm{M^+\,h_m\,(H_2O)\,;aq}) + \mu^{\#}\,(\mathrm{X^-\,h_X\,(H_2O)\,;aq}) \\ + \mathrm{R\,T\,ln}\left\{\gamma_+(\mathrm{II})\,\gamma_-(\mathrm{II})\right\}$$

Using the definition of $\mu''\,(\mathrm{M^+;I})$ and $\mu''\,(\mathrm{X^-;I})$ and equations (e) and (f) for description (II),

$$\frac{\mathrm{m}\,(\mathrm{M^+;I})\;\mathrm{m}\,(\mathrm{X^-;I})}{\mathrm{m}\,(\mathrm{M^+;II})\;\mathrm{m}\,(\mathrm{X^-;II})} = \\ \frac{\mathrm{n_j}}{\mathrm{M_1\,n_1}}\,\frac{\mathrm{M_1}\;[\mathrm{n_1} - (\mathrm{h_m + h_X})\;\mathrm{n_j}]}{\mathrm{n_j}}\,\frac{\mathrm{n_j}}{\mathrm{M_1\,n_1}}\,\frac{\mathrm{M_1}\;[\mathrm{n_1} - (\mathrm{h_m + h_X})\;\mathrm{n_j}]}{\mathrm{n_j}}$$

Thus,

$$\frac{\mathrm{m}\,(\mathrm{M^+;I})\;\mathrm{m}\,(\mathrm{X^-;I})}{\mathrm{m}\,(\mathrm{M^+;II})\;\mathrm{m}\,(\mathrm{X^-;II})} = [1 - (\mathrm{h_m + h_X})\;\mathrm{M_1\,m_j}]^2$$

Therefore,

$$
\begin{aligned}
&\mu^{\#\prime}\left(\mathrm{M}^{+};\mathrm{aq}\right)+\mu^{\#\prime}\left(\mathrm{X}^{-};\mathrm{aq}\right)+2\,\phi\,\mathrm{R\,T}\,\ln\left[1-\mathrm{M}_1\,\mathrm{m_j}\,\left(\mathrm{h_m}+\mathrm{h_X}\right)\right]\\
&\quad+\mathrm{R\,T}\,\ln\left\{\gamma_{+}(\mathrm{I})\,\gamma_{-}(\mathrm{I})\right\}\\
&=-\left(\mathrm{h_m}+\mathrm{h_X}\right)\,\left\{\mu_1^{*}(\ell)-2\,\phi\,\mathrm{R\,T\,M}_1\,\mathrm{m_j}\right\}\\
&\quad+\mu^{\#*}\left(\mathrm{M}^{+};\mathrm{h_m H_2O};\mathrm{aq}\right)+\mu^{\#\#}\left(\mathrm{X}^{-};\mathrm{h_X H_2O};\mathrm{aq}\right)+\mathrm{R\,T}\,\ln\left\{\gamma_{+}(\mathrm{II})\,\gamma_{-}(\mathrm{II})\right\}
\end{aligned}
$$

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1.10.15: Gibbs Energies- Salt Solutions- Electric Neutrality

The solid crystalline salt NaCl comprises a lattice of sodium $\mathrm{Na^+}$ and chloride $\mathrm{Cl^-}$ ions. The charge number on each sodium ion, $\mathrm{z_+}$, is $+1$; the charge number on each chloride ion, $\mathrm{z_-}$, is -1. The amount of sodium ions ν_+ produced by one mole of sodium chloride is 1 mol. The amount of chloride ions ν_- produced by one mole of sodium chloride is 1 mol. The electric charge on the sodium ions in one mole of sodium chloride is $(\mathrm{v_+\, z_+\, N_A\, e})$ C where e is the unit charge and $\mathrm{N_A}$ is the Avogadro constant. The product $(\mathrm{N_A\, e})$ $\{= [\mathrm{C}].[\mathrm{mol}]^{-1}\}$ is the Faraday constant \(\left{=\left[\mathrm{C} \mathrm{mol}\^{-1}\right]\right\}\). Similarly the electric charge on the chloride ions in 1 mol of sodium chloride equals, $(\mathrm{v_-\, z_-\, N_A\, e})$ C. The total electric charge on one mole of solid sodium chloride equals $[(\mathrm{v_+\, z_+\, N_A\, e}) + (\mathrm{v_-\, z_-\, N_A\, e})]\, C$ which equals zero.

We make these points in order to highlight the fact that the total electric charge on 1 mol of sodium cations (in for example 53 g of common salt) is enormous, being 96 500 C. Very few laboratories can handle such enormous electric charges. Chemists cope because the electric neutrality condition always operates [1]. When we set down equations describing the properties of salt solutions we ensure that the electric neutrality condition is not violated. However when we turn to the task of developing molecular models for these systems we recognize the magnitude of the forces involved.

Footnotes

[1] One model of Utopia is a society when there are equal number of men and women. It is interesting to note that from the perspective of each male, the Utopian society has a majority of women. Similarly each woman lives in a male dominated society. Life is the same for ions.

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1.10.16: Gibbs Energies- Salt Solutions- Born Equation

The Born Equation [1] is based on a BBB model, “brass balls in a bathtub” [2]. The solvent is treated as a dielectric continuum characterised at temperature T and pressure p by its relative permittivity ε_r. The ions are treated as hard non-polarizable spheres, having radius r_j. The Born Equation describes the difference in thermodynamic properties of a mole of i-ions forming a perfect gas and a mole of j-ions in an ideal solution at temperature T and pressure p. The calculation is not straightforward [3-5]. What emerges is the difference in Helmholtz energies (at constant T and V) for a mole of j ions in incompressible liquid phases. The calculated quantities refer to the energies associated with the electric fields over the limits $r_j \leq r \leq \infty$. In these terms the Born Equation describes the electrical part of the change in chemical potential on transferring an ion from the gas phase, permittivity ε_0, to a solvent, relative (electric) permittivity ε_r. In effect the Born Equation yields parameters characterizing the difference between the properties of one mole of j ions in ideal systems having equal concentrations at fixed T and p [6].

$$= -N_A \left(z_j\, e\right)^2 \left[1 - \left(1/\varepsilon_r\right)\right] /8\,\pi\, r_j\, \varepsilon_0$$

Similarly for transfer of one mole of j ions from an ideal solution in solvent $\mathrm{s_1}$ to an ideal solution in solvent $\mathrm{s_2}$, the transfer chemical potential is given by the Born Equation assuming r_j is independent of solvent.

$$\mathrm{N_A}\ \left(\mathrm{z_j\, e}\right)^2 \left[\left(1/\varepsilon_\mathrm{r}(\mathrm{s2})\right) - \left(1/\varepsilon_\mathrm{r}(\mathrm{s1})\right)\right] /8\,\pi\, \mathrm{r_j}\, \varepsilon_0$$

Many attempts have been made to modify the Born Equation in order to attain agreement between theory and measured thermodynamic ionic properties, particularly in the case of aqueous salt solutions. A common concern is the extent to which near-neighbor water molecules form an electrostricted layer [7] around ions in solution, namely a layer of solvent molecules having dielectric properties which differ from those of the pure solvent at the same temperature and pressure [8 - 11]. A common concern in this subject is the definition of the ionic radius for a given ion [12 - 16]. There is no agreement concerning a set of ‘absolute’ ionic radii. As Conway pointed out in 1966, ‘ …theories .. based on the Born equation seem to have reached an asymptotic level of usefulness..’ [17].

Nevertheless correlations involving thermodynamic properties of salt solutions play an important role.

Standard partial molar entropies for alkali metal halides in various solvents are linear functions of the corresponding entropies in aqueous solution [18]. A similar correlation is reported for ionic entropies in mixed aqueous solvents and the corresponding entropies in aqueous solutions [19]. With reference to enthalpies, the analysis also suffers from the fact that the ionic radius is sensitive to temperature [20].

Footnotes

[1] M. Born, Z. Phys., 1920, **1**, 45.

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[6]

$$\begin{aligned} &Delta(\mathrm{pfg} \rightarrow \mathrm{s\,ln})\mu_\mathrm{j} = \left[\mathrm{mol}^{-1}\right]\ \left[\mathrm{C}\right]^2 \{[1] - [1]\}/[1]\,[1]\,[\mathrm{m}]\ \left[\mathrm{Fm}^{-1}\right] = \\ &[\mathrm{mol}]^{-1}\ \left[\mathrm{A}^2\ \mathrm{s}^2\right]/[\mathrm{m}]\ \left[\mathrm{A}^2\ \mathrm{s}^4\ \mathrm{kg}^{-1}\ \mathrm{m}^{-3}\right] = \left[\mathrm{mol}^{-1}\right]\ \left[\mathrm{kgm}^2\ \mathrm{s}^{-2}\right] = \left[\mathrm{Jmol}^{-1}\right] \end{aligned}$$

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1.10.17: Gibbs Energies- Salt Solutions- Lattice Models

Lattice models for salt solutions have attracted and continue to attract interest [1]. Ions in a salt solution are regarded as occupying lattice sites, the lattice parameter increasing as a solution is diluted; solvent molecules occupy the interstices of the lattice. This model for salt solutions generates interest because the distribution of ions about a central reference j-ion is therefore known. This theory requires that $\ln \gamma_{\pm}$ is a linear function of $(m_i/m^0)^{1/3}$ for salt-i; the cube-root law. This dependence is observed for reasonably concentrated salt solutions [2]. Unfortunately convincing evidence for lattice structures is not forthcoming. For example, the electrical conductivities of salt solutions cannot be understood in terms of lattice structures.

Footnotes

[1]

a. J. C. Ghosh, J. Chem. Soc., 1918, 449, 627, 707, 790.
b. H. S. Frank and P. T. Thompson, in Structure of Electrolytic Solutions, ed. W. J. Hamer, Wiley, New York, 1959, p.113.
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f. B. N. Ghosh, J. Ind. Chem. Soc., 1983,**60**, 141, 607; 1981,**58**, 675; 1984,**61**, 213.
g. I. Horsak and I. Slama, Collect. Czech. Chem. Commum., 1987,**52**, 1672.

[2] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd. edition revised,1965, pp. 226

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1.10.18: Gibbs Energies- Salt Solutions- Debye-Huckel Equation

The electric potential ϕ_j (at ion-j; ion-ion interaction) describes the electric potential at a given reference j-ion arising from all other i-ions in solution. The contribution to the chemical potential of one mole of j-ions is obtained using the Guntleberg charging process. Thus,

$$\Delta\mu_{\mathrm{j}}(\text{ ion } -\mathrm{j};\text{ ion } -\text{ ion int eractions }) = \int_0^{\mathrm{z_j\,e}} \varphi_{\mathrm{j}}(\text{ at ion } -\mathrm{j};\text{ ion } -\text{ ion })\,\mathrm{d}\,(\mathrm{z_j\,e})$$

Hence[1],

$$\Delta\mu_{\mathrm{j}}(\text{ ion } -\mathrm{j};\text{ ion } -\text{ ion int eractions }) = -\frac{(\mathrm{z_j\,e})^2\,\mathrm{N_A}}{8\,\pi\,\varepsilon_0\,\varepsilon_{\mathrm{r}}}\,\frac{\kappa}{1+\kappa\,\mathrm{a}}$$

The charge-charge interactions are the only source of deviations in the properties of a given solution from ideal. Then for ion-j,

$$\ln(\gamma_{\mathrm{j}}) = \Delta\mu_j(\text{ ion } -\mathrm{j} <-\longrightarrow> \text{ ion atmos. })/\mathrm{R\,T}$$

Hence for the ionic activity coefficient γ_j,

$$\ln(\gamma_{\mathrm{j}}) = -\frac{(\mathrm{z_j\,e})^2\,\mathrm{N_A}}{8\,\pi\,\varepsilon_0\,\varepsilon_{\mathrm{r}}\,\mathrm{R\,T}}\,\frac{\kappa}{1+\kappa\,\mathrm{a}}$$

Ionic activity coefficients have no practical significance. We require an equation for the mean ionic activity coefficient for a salt in solution. For one of mole of salt in solution,

$$v\,\ln(\gamma_{\pm}) = v_+\,\ln(\gamma_+) + v_-\,\ln(\gamma_-)$$

or,

$$\ln(\gamma_{\pm}) = \frac{1}{(v_+ + v_-)}\,[v_+\,\ln(\gamma_+) + v_-\,\ln(\gamma_-)]$$

Hence

$$\ln(\gamma_{\pm}) = -\frac{1}{(v_+ + v_-)}\,\left[v_+\,z_+^2 + v_-\,z_-^2\right]\,\left[\frac{e^2\,N_A}{8\,\pi\,\varepsilon_0\,\varepsilon_{\mathrm{r}}\,RT}\,\frac{\kappa}{(1+\kappa\,a)}\right]$$

Or[2,3],

$$\ln(\gamma_{\pm}) = -\left[\frac{|z_+\,z_-|\;e^2\,N_A}{8\,\pi\,\varepsilon_0\,\varepsilon_t\,RT}\,\frac{K}{(1+K\,a)}\right]$$

In this connection the distance 'a' characterises both cations and anions in the salt. In the Debye-Huckel Limiting Law (DHLL) the term $(1+\kappa\,a)$ is approximated to unity thereby assuming that $(1 >> K\,a)$. Then using the term $\mathrm{S_\gamma}$, for a 1:1 salt equation (h) is rewritten as follows.

$$\ln(\gamma_{\pm}) = -|\mathrm{z_+\,z_-}|\;\mathrm{S_\gamma}\;(\mathrm{m_j/m^0})^{1/2}\,/\left[1+\mathrm{b}\;(\mathrm{m_j/m^0})^{1/2}\right]$$

where

$$\mathrm{b} = \beta\,\mathrm{a}$$

and [4]

$$\beta = \left[\frac{2\,\mathrm{e}^2\,\mathrm{N_A^2}\,\rho_1^*(\ell)\,\mathrm{m}^0}{\varepsilon_0\,\varepsilon_{\mathrm{r}}\,\mathrm{R\,T}}\right]^{1/2}$$

For aqueous solutions at ambient pressure and 298.15 K, $\beta = 3.285\times10^9\ \mathrm{m}^{-1}$ [5].

The quantity b depends on a distance parameter [6] 'a' which characterises salt j and reflects the role of repulsion between ions in determining the chemical potentials of a salt in solution. Hence with increase in distance 'a' so the denominator increases and

$\ln(\gamma_j)$ is not so strongly negative as predicted by the DHLL. For large 'a' and high ionic strengths, the salts are not stabilised to the extent required by the DHLL. The integrated form of the Gibbs-Duhem equation yields an equation for $(\phi - 1)$ in terms of molality m_j [7]. Thus,

$$m_j\,(1-\phi) = -\int_0^{m(j)} m_j\,d\ln(\gamma_\pm)$$

Hence, [6]

$$(1-\phi) = [|z_+\,z_-|\;S_\gamma/3]\;\left(m_j/m^0\right)^{-1}\;\sigma(x)$$

and

$$\sigma(x) = (3/x^3)\;\left[(1+x) - (1+x)^{-1} - 2\,\ln(1+x)\right]$$

Then the excess molar Gibbs energy for a solution containing a 1:1 salt is given by equation (o).

$$G_m^E = 2\,R\,T\,S_\gamma\,m_j^{3/2}\;\left(m^0\right)^{-1}\;\left[\sigma(x)/3 - (1+x)^{-1}\right]$$

Footnotes

[1]

$$\begin{aligned}\Delta\mu_j(---) &= \frac{[As]^2\;[mol^{-1}]}{[1]\;[Fm^{-1}]\;[1]}\;\frac{[m^{-1}]}{\{[1]+[m^{-1}]\;[m]\}}\\ &= \frac{[A^2\,s^2]\;[mol^{-1}]}{[AsV^{-1}]} = \frac{[A^2\,s^2]\;[mol^{-1}]}{[AsAsJ^{-1}]} = [Jmol^{-1}]\end{aligned}$$

[2] Condition of electric neutrality; $v_+\,z_+ = -v_-\,z_-$ or, $v_- = -v_+\,z_+/z_-$

Then,

$$\begin{aligned}&\frac{1}{(v_+ + v_-)}\;\left[v_+\,z_+^2 + v_-\,z_-^2\right]\\ =&\left[\frac{1}{v_+ - v_-\,z_+/z_-}\right]\;\left[v_+\,z_+^2 - v_+\,z_+\,z_-\right] = \frac{z_-}{(z_- - z_+)}\;\left[z_+^2 - z_+\,z_-\right]\\ =&-z_+\,z_- = |z_+\,z_-|\end{aligned}$$

[3] $\ln(\gamma_\pm) = \frac{[1]\;[As]^2\;[mol]}{[1]\;[1]\;[AsJ^{-1}As]\;[Jmol^{-1}\;K^{-1}]\;[K]}\;\frac{[m^{-1}]}{\{1+[m^{-1}]\;[m]\}} = [1]$

[4]

$$\begin{aligned}\beta &= \left\{[1]\,[C]^2\;\left[mol^{-1}\right]^2\;\left[kgm^{-3}\right]\;\left[molkg^{-1}\right]\right\}^{1/2}\\ /&\left\{\left[J^{-1}C^2\;m^{-1}\right]\;[1]\;\left[JK^{-1}\;mol^{-1}\right]\;[K]\right\}^{1/2} = \left[m^{-1}\right]\end{aligned}$$

[5] For DH parameters for aqueous solutions to high T and p, see D. J. Bradley and K. S. Pitzer,J. Phys.Chem.,1979,**83**,1599;1983;**87**,3798.

[6] Parameter 'a' is sometimes called 'ion size' . But as S. Glasstone [Introduction to Electrochemistry, D.van Nostrand, New Jersey, 1943, page 145, footnote] points out 'the exact physical significance cannot be expressed precisely'. Nevertheless an important consideration is the relative sizes of ions and solvent molecules; B. E. Conway and R. E. Verrall, J.Phys.Chem.,1966, **70**,1473.

[7] From equation (i) when by definition $x = b\;(m_j/m^0)^{1/2}$ and $k = |Z_+\,Z_-|\;S_\gamma/b$

Hence,

$$\begin{aligned}&\ln(\gamma_\pm) = -(b\,k)\,(x/b)/(1+x) = -k\,x/(1+x)\\ &d\ln(\gamma_\pm) = -k\;\left\{[1/(1+x)] - \left[x/(1+x)^2\right]\right\}\;dx = -k\;\left\{[1+x-x]/[1+x]^2\right\}\;dx\\ &d\ln(\gamma_\pm) = -k\,dx/[1+x]^2\end{aligned}$$

Therefore,

$$(1-\phi)\, m_j = -\int_0^x m_j \left\{-k/(1+x)^2\right\}\, dx$$

Or, $(1-\phi) = (k/x^2)\, \int_0^x \left\{x^2/(1+x)^2\right\}\, dx$

Standard integral:

$$\int_0^x \left\{x^2/(a\,x+b)^2\right\}\, dx =$$
$$\left\{(a\,x+b)/a^3\right\} - \left\{b^2/a^3\,(a\,x+b)\right\} - \left(2\,b/a^3\right)\, \ln(a\,x+b)$$

With $a = b = 1$,

$$\int_0^x \left\{x^2/(1+x)^2\right\}\, dx = (1+x) - [1/(1+x)] - 2\, \ln(1+x)$$

Thus,

$$(1-\phi) = (k\,x/3)\, \left\{\left(3/x^3\right)\, \left[(1+x) - (1+x)^{-1} - 2\, \ln(1+x)\right]\right.$$

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1.10.19: Gibbs Energies- Salt Solutions- Debye-Huckel Limiting Law

According to the Debye-Huckel analysis the mean ionic activity coefficient is given by equation (a).

$$\ln\left(\gamma_{\pm}\right) = -\left[\frac{\left|z_{+}\,z_{-}\right|\,e^{2}\,N_{A}}{8\,\pi\,\varepsilon_{0}\,\varepsilon_{t}\,RT}\,\frac{K}{(1+K\,a)}\right]$$

In the DHLL the term $(1+\kappa\,a)$ is approximated to unity thereby assuming that $(1>>\kappa\,a)$. By definition

$$\mathrm{S}_{\gamma} = \left[\frac{2\,\pi\,\mathrm{N_A}\,\mathrm{M_1}\,\mathrm{m}^{0}}{\mathrm{V}_{1}^{*}(\ell)}\right]^{1/2}\,\left[\frac{\mathrm{e}^{2}\,\mathrm{N_A}}{4\,\pi\,\varepsilon_{0}\,\varepsilon_{\mathrm{r}}\,\mathrm{R\,T}}\right]^{3/2}$$

Then[1]

$$\ln\left(\gamma_{\pm}\right) = -\left|z_{+}\,z_{-}\right|\,S_{\gamma}\,\left(m_{j}/m^{0}\right)^{1/2}$$

The practical osmotic coefficient for quite dilute salt solutions is also a linear function of $(\mathrm{m}_{j})^{1/2}$.$Indeed\backslash($$\phi$ and $\ln\left(\gamma_{\pm}\right)$ are simply related.

$$1-\phi = -(1/3)\,\ln\left(\gamma_{\pm}\right)$$

Footnotes

[1] From,

$$\mathrm{S}_{\gamma} = \frac{\mathrm{e}^{3}\,\left[2\,\mathrm{N_A}\,\rho_{1}^{*}(\ell)\right]^{1/2}}{8\,\pi\,\left[\varepsilon_{0}\,\varepsilon_{\mathrm{r}}\,\mathrm{k\,T}\right]^{3/2}}$$

Then, $\frac{1}{\pi} = \frac{\pi^{1/2}}{\pi^{3/2}}$ and $\frac{1}{8} = \frac{1}{4^{3/2}}$

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1.10.20: Gibbs Energies- Salt Solutions- DHLL- Derived Parameters

Granted that the DHLL forms a starting point for understanding the role of ion-ion interactions in aqueous solutions, we use the DHLL to explain the impact of these interactions on related properties such as volumes and enthalpies. We write the Debye-Huckel coefficient as a function of three variables:

i. the molar volume of the solvent $\mathrm{V}_1^*(\ell)$,
ii. the relative permittivity of the solvent, ε_r and
iii. the temperature.

Here we take account of the fact that $\mathrm{V}_1^*(\ell)$ and ε_r depend on both temperature and pressure.

$$S_\gamma = \left[\frac{2\,\pi\,\mathrm{N_A}\,\mathrm{M_1}\,\mathrm{m}^0}{\mathrm{V}_1^*(\ell)}\right]^{1/2}\,\left[\frac{\mathrm{e}^2\,\mathrm{N_A}}{4\,\pi\,\varepsilon^0\,\varepsilon_\mathrm{r}\,\mathrm{R}\,\mathrm{T}}\right]^{3/2}$$

S_γ is written in the following form.

$$\mathrm{S}_\gamma = \mathrm{E}\,[\mathrm{V}_1^*(\ell)]^{-1/2}\,(\varepsilon_\mathrm{r})^{-3/2}\,(\mathrm{T})^{-3/2}$$

where

$$\mathrm{E} = \left[2\,\pi\,\mathrm{N_A}\,\mathrm{M_1}\,\mathrm{m}^0\right]^{1/2}\,\left[\frac{\mathrm{e}^2\,\mathrm{N_A}}{4\,\pi\,\varepsilon^0\,\mathrm{R}}\right]^{3/2}$$

Hence[1]

$$\mathrm{S}_\gamma = \mathrm{E}\,\mathrm{F}$$

where

$$\mathrm{F} = [\mathrm{V}_1^*(\ell)]^{-1/2}\,(\varepsilon_\mathrm{r})^{-3/2}\,(\mathrm{T})^{-3/2}$$

In terms of our interest in the dependence of $\mu_\mathrm{j}(\mathrm{aq})$ for salt j on temperature leading to partial molar enthalpies we require $[\partial \mathrm{S}_\gamma/\partial \mathrm{T}]_\mathrm{p}$ which is calculated using the dependences of both $\mathrm{V}_1^*(\ell)$ and ε_r on temperature yielding $(\partial \mathrm{F}/\partial \mathrm{T})_\mathrm{p}$. For partial molar isobaric heat capacities we require the second differential $(\partial^2\,\mathrm{F}/\partial \mathrm{T}^2)_\mathrm{P}$. The predicted dependence by DHLL of the partial molar volume $\mathrm{V}_\mathrm{j}(\mathrm{aq})$ on salt molality involves the derivative $(\partial \mathrm{F}/\partial \mathrm{p})_\mathrm{T}$.

Calculations are considerably helped using a PC in conjunction with equations describing the $\mathrm{T}-\mathrm{p}$ dependences of $\mathrm{V}_1^*(\ell)$ and ε_r.

Footnotes

[1] $\mathrm{E} = [[1]\,[1]\,\left[\mathrm{mol}^{-1}\right]\,\left[\mathrm{kgmol}^{-1}\right]\,\left[\mathrm{molkg}^{-1}\right]]^{1/2}\,\left[\frac{[\mathrm{C}]^2\,\left[\mathrm{mol}^{-1}\right]}{[1]\,[1]\,\left[\mathrm{C}^2\,\mathrm{J}^{-1}\,\mathrm{m}^{-1}\right]\,\left[\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}\right]}\right]^{3/2}$

or, $\mathrm{E} = [\mathrm{mol}]^{-1/2}\,[\mathrm{m}]^{3/2}\,[\mathrm{K}]^{3/2} = \left[\mathrm{m}^3\,\mathrm{mol}^{-1}\right]^{1/2}\,[\mathrm{K}]^{3/2}$

and $\mathrm{F} = \left[\mathrm{m}^3\,\mathrm{mol}^{-1}\right]^{-1/2}\,[1]^{-3/2}\,[\mathrm{K}]^{-3/2}$

Hence, $\mathrm{S}_\gamma = \left[\mathrm{m}^3\,\mathrm{mol}^{-1}\right]^{1/2}\,[\mathrm{K}]^{3/2}\,\left[\mathrm{m}^3\,\mathrm{mol}^{-1}\right]^{-1/2}\,[1]^{-3/2}\,[\mathrm{K}]^{-3/2} = [1]$

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1.10.21: Gibbs Energies- Salt Solutions- DHLL- Empirical Modifications

The success of equations based on the Debye-Huckel equations is often modest and so attempts are made to describe quantitatively the dependences of ϕ, $\ln(\gamma_{\pm})$ and $G^{E}_{m}(aq;T;p)$ on m_j to higher molalities. In most cases attempts are made to moderate the stabilization of the salt with increasing ionic strength. The obvious procedure centres on incorporating a denominator into the DHLL as illustrated by the Guntleberg equation.

$$\ln(\gamma_{\pm}) = -|z_{+}\,z_{-}|\;S_{\gamma}\;\left(I/m^{0}\right)^{1/2} / \left\{1+\left(I/m^{0}\right)^{1/2}\right\}$$

The Guggenheim Equation starts with equation (a) and adds a further term, linear in ionic strength.

$$\ln(\gamma_{\pm}) = -\left[|z_{+}\,z_{-}|\;S_{\gamma}\;\left(I/m^{0}\right)^{1/2} / \left\{1+\left(I/m^{0}\right)^{1/2}\right\}\right] + b\;\left(I/m^{0}\right)$$

The quantity 'b' is characteristic of the salt. Another obvious development uses the same approach in the context of the DHLL. An interesting equation takes the following form for the solution containing a salt j.

$$\ln(\gamma_{\pm}) = -\left[|z_{+}\,z_{-}|\;S_{\gamma}\;\left(m_{j}/m^{0}\right)^{1/2}\right] + B\;\left(m_{j}/m^{0}\right)$$

Here B describes the role of ion size and the impact of cosphere-cosphere interactions specific to a particular salt.

In most approaches, the starting point in an equation for $\ln(\gamma_{\pm})$ as a function of ionic strength, the equation for the dependence of ϕ on ionic strength being obtained using the integral of equation (c). An interesting approach suggested by Bronsted starts out with a virial equation for $1-\phi$ in terms of molality m_j.

$$1-\phi = \alpha\;\left(m_{j}/m^{0}\right)^{1/2} + \beta\;\left(m_{j}/m^{0}\right)$$

Hence [1]

$$\ln(\gamma_{\pm}) = -3\,\alpha\;\left(m_{j}/m^{0}\right)^{1/2} - 2\,\beta\;\left(m_{j}/m^{0}\right)$$

Footnote

[1] From

$$\ln(\gamma_{\pm}) = (\phi-1) + \int_{0}^{m_j} (\phi-1)\,d\ln m_j$$

$$\ln(\gamma_{\pm}) = (\phi-1) - \int_{0}^{m_j} \left[\left\{\alpha\;\left(m_{j}/m^{0}\right)^{1/2} + \beta\;\left(m_{j}/m^{0}\right)\right\}/m_{j}\right]\,dm_{j}$$

$$\ln(\gamma_{\pm}) = (\phi-1) - \int_{0}^{m_j} \left[\left\{\alpha/m_j\,m^{0}\right)^{1/2}\right\} + \left\{\beta/m^{0}\right\}\Big]\,d_j$$

$$\ln(\gamma_{\pm}) = (\phi-1) - \left[2\,\alpha\;\left(m_j/m^{0}\right)^{1/2} + \beta\;\left(m_j/m^{0}\right)\right]_{0}^{m_j}$$

$$\ln(\gamma_{\pm}) = -\alpha\;\left(m_{j}/m^{0}\right)^{1/2} - \beta\;\left(m_{j}/m^{0}\right) - 2\,\alpha\;\left(m_{j}/m^{0}\right)^{1/2} - \beta\;\left(m_{j}/m^{0}\right)$$

$$\ln(\gamma_{\pm}) = -3\,\alpha\;\left(m_{j}/m^{0}\right)^{1/2} - 2\,\beta\;\left(m_{j}/m^{0}\right)$$

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1.10.22: Gibbs Energies- Salt Solutions- Solvent

A given salt solution contains a 1:1 salt j (e.g. NaCl) in which the salt, chemical substance j, completely dissociates into ions. In other words, the total molality of solutes equals $2\,m_j$. By definition the chemical potential of water in this aqueous solution, $\mu_1(\mathrm{aq})$ (at fixed temperature and pressure, the latter being ambient and hence close to the standard pressure p^0) is given by equation (a).

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - 2\,\phi\,\mathrm{R\,T\,M_1\,m_j}$$

For the corresponding ideal solution, $\phi = 1.0$ at all T and p, Hence,

$$\mu_1(\mathrm{aq;id}) = \mu_1^*(\ell) - 2\,\mathrm{R\,T\,M_1\,m_j}$$

Just as for solutions containing neutral solutes, the minus sign in equation (b) means that added salt stabilizes the solvent in an ideal solution; $\mu_1(\mathrm{aq;id}) < \mu_1^*(\ell)$.

For water in an aqueous salt solution containing salt j, molality m_j, where each mole of salt forms v moles of ions with complete dissociation, the chemical potential of the solvents is given by equation (c).

$$\mu_1(\mathrm{aq}) = \mu_1^*\left(\ell;\mathrm{p}^0\right) - \mathrm{v}\,\phi\,\mathrm{R\,T\,M_1\,m_j} + \int_{\mathrm{p}(0)}^{\mathrm{p}} \mathrm{V}_1^*(\ell)\,\mathrm{dp}$$

For the ideal dilute solution, $\phi = 1.0$. Here $\mu_1^*\left(\ell,\mathrm{p}^0\right)$ is the standard chemical potential of water at temperature T. Alternatively we may switch the reference chemical potential for the solvent to the pure liquid at the same pressure [1,2].

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^*(\ell;\mathrm{T;p}) - \mathrm{v}\,\phi\,\mathrm{R\,T\,M_1\,m_j}$$

Footnotes

[1] For relevant Tables see;' R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd edn.(revised), Butterworths, London, 1965, Appendix 8.

[2] The impact of salts on osmotic coefficients is illustrated by the properties of aqueous solutions containing alkylammonium salts.

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1.10.23: Gibbs Energies- Salt Solutions- Excess Gibbs Energies

A given salt solution contains a single salt j which completely dissociates to form ν moles of ions from one mole of salt. Then the chemical potential of the salt j in aqueous solution at temperature T and pressure p is given by equation (a).

$$\mu_j(aq) = \mu_j^0(aq) + v\,RT\,\ln\left(Q\,m_j\,\gamma_\pm/m^0\right) + \int_{p^0}^{p} V_j^\infty(aq)\,dp$$

Here $\mu_j^0(\mathrm{aq})$ is the chemical potential of the salt in solution at the same temperature and the standard pressure where molality $\mathrm{m_j} = 1\ \mathrm{mol\ kg^{-1}}$ and mean ionic activity coefficient $\gamma_\pm = 1$. The chemical potential of water in aqueous solution at temperature T and pressure p is given by equation (b) where ϕ is the practical osmotic coefficient [1-3],

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - \mathrm{v}\,\phi\,\mathrm{R\,T\,M_1\,m_j} + \int_{\mathrm{p}}^{\mathrm{p}} \mathrm{V_1^*}(\ell)\,\mathrm{dp}$$

If we confine our attention to the properties of solutions at ambient pressure (which is very close to the standard pressure) then we can ignore the integrals in equations (a) and (b). Hence the Gibbs energy of the solution at the same T and p prepared using 1 kg of water is given by equation (c).

$$\begin{aligned}\mathrm{G\,(aq;\,w_1 = 1\ kg)} = (1/\mathrm{M_1})\ [\mu_1^*(\ell) - \mathrm{v}\,\phi\,\mathrm{R\,T\,M_1\,m_j}] \\ + \mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{v\,R\,T\ ln\left(Q\,m_j\,\gamma_\pm/m^0\right)}\right]\end{aligned}$$

As for solutions containing neutral solutes we cannot put a number value to $\mathrm{G\,(aq;\,w_1 = 1\ kg)}$. If the properties of this salt solution are in fact ideal (in a thermodynamic sense) then $\mathrm{G\,(aq;\,w_1 = 1\ kg : id)}$ is given by equation (d).

$$\begin{aligned}\mathrm{G\,(aq;\,id;\,w_1 = 1\ kg)} =& (1/\mathrm{M_1})\ [\mu_1^*(\ell) - \mathrm{v\,R\,T\,M_l\,m_j}] \\ &+ \mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{v\,R\,T\ ln\left(Q\,m_j\,\gamma_\pm/m^0\right)}\right]\end{aligned}$$

Hence in the case where $j = \mathrm{NaCl}$, $\nu = 2$ and $\mathrm{Q} = 1$. In the next stage we use differences between $\mathrm{G\,(aq;\,w_1 = 1\ kg)}$ and $\mathrm{G\,(aq;\,id;\,w_1 = 1\ kg)}$ to define excess Gibbs energies for a solution prepared using 1 kg of water. Then

$$\mathrm{G^E = G\,(aq;\,w_1 = 1\ kg) - G\,(aq;\,id;\,w_1 = 1\ kg)}$$

For salt j,

$$\mathrm{G^E = V\,m_j\,R\,T\ [1 - \phi + \ln\,(\gamma_\pm)]}$$

According to the Gibbs-Duhem for a solution at constant temperature and constant pressure,

$$\mathrm{n_1\,d\mu_1(aq) + n_j\,d\mu_j(aq) = 0}$$

Hence for salt j,

$$\begin{aligned}&(1/\mathrm{M_1})\ \mathrm{d}\,[\mu_1^*(\ell) - \mathrm{v}\,\phi\,\mathrm{R\,T\,M_1\,m_j}] \\ &+\mathrm{m_j\,d}\,\left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{v\,R\,T\ ln\left(Q\,m_j\,\gamma_\pm/m^0\right)}\right] = 0\end{aligned}$$

We are concerned with the dependence of chemical potential on the molality of salt. Thus the amount of solvent and, for the salt, both Q and v are fixed. Hence

$$\mathrm{d}\,[-\phi\,\mathrm{m_j}] + \mathrm{m_j\,d}\,\left[\ln\left(\mathrm{m_j}\,\gamma_\pm/\mathrm{m^0}\right)\right] = 0$$

Hence,

$$-\phi\,dm_j - m_j\,d\phi + m_j\,dm_j/m_j + m_j\,d\ln\,(\gamma_t) = 0$$

Then,

$$(\phi - 1)\,dm_j + m_j\,d\phi = m_j\,d\ln\,(\gamma_\pm)$$

Hence we obtain an equation for $\ln\,(\gamma_\pm)$ in terms of the dependence of $(\phi - 1)$ on molality bearing in mind that $\ln\,(\gamma_\pm)$ equals zero and ϕ equals 1 at '$\mathrm{m}_j = 0$'.

$$\ln(\gamma_{\pm}) = (\phi - 1) + \int_0^{m_j} (\phi - 1)\, d\ln(m_j)$$

From equation (f), the dependence of G^E on m_j is given by equation (m).

$$(1/V\,R\,T)\,dG^E/dm_j = [1 - \phi + \ln(\gamma_{\pm})] - m_j\,(d\phi/dm_j) + m_j\,d\ln(\gamma_{\pm})/dm_j = 0$$

But according to equation (i),

$$-\phi - m_j\,d\phi/dm_j + 1 + m_j\,d\ln(\gamma_{\pm})/dm_j = 0$$

Hence[4],

$$\ln(\gamma_{\pm}) = (1/V\,R\,T)\,dG^E/dm_j$$

Footnotes

[1] Compilation of Data for polyvalent electrolytes; R. N. Goldberg, B. R. Staples, R. L. Nuttall and R. Arbuckle, NBS Special Publication 485, 1977.

[2] Thermal Properties of Aqueous Univalent –Univalent Electrolytes, V.B.Parker, NBS, 2, 1965.

[3] J.-L. Fortier and J. E. Desnoyers, J. Solution Chem.,1976,**5**,297.

[4]

$$\ln(\gamma_{\pm}) = \left[\frac{1}{[1]\ [JK^{-1}\ mol^{-1}]\ [K]}\right]\left[\frac{Jkg^{-1}}{mol\ kg^{-1}}\right] = [1]$$

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1.10.24: Gibbs Energies- Salt Solutions- Pitzer's Equations

The Debye-Huckel treatment of the properties of salt solutions is based on a linearization of the Botzmann Equation leading to an equation for the radial distribution function, $g_{ij}(r)$. If a further term is taken into the expansion, the equation for $g_{ij}(r)$ takes the following form [1].

$$g_{ij}(r) = 1 - q_{ij} + (q_{ij}^2/2)$$

When equation (a) was tested against the results of a careful Monte Carlo calculation the conclusion was drawn that the three-term equation is good approximation [2]. The result is a set of equations for both the practical osmotic coefficient ϕ and mean ionic activity coefficient for the salt in a solution having ionic strength I [3,4]. The theory has been extended to consider the properties of salt solutions at high T and p [5,6]. In fact key parameters in Pitzer equations covering extensive ranges of T and p have been extensively documented [7]. The Pitzer treatment has been extended to a consideration of the properties of mixed salt solutions [8].

Footnotes

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1.10.25: Gibbs Energies- Salt Solutions- Cosphere - Cosphere Interactions

The Debye-Huckel equations form the starting point for detailed analyses of the properties of salt solutions. An interesting method examines excess thermodynamic properties of salt solutions and their dependence on salt molality [1]. For an aqueous solution containing a 1:1 salt in 1 kg of solvent, the excess Gibbs energy G^E is given by equation (a).

$$G^E = 2\,R\,T\,m_j\,[1 - \phi + \ln \gamma_\pm]$$

The corresponding excess molar Gibbs energy is given by equation (b).

$$G_m^E = 2\,R\,T\,[1 - \phi + \ln \gamma_\pm]$$

The corresponding excess molar enthalpy $H_m{}^E$ is obtained from calorimetric data. Hence the molar excess entropy is calculated using equation (c).

$$G_m^E = H_m^E - T\,S_m^E$$

A common observation is that $H_m{}^E$ and $T.S_m{}^E$ are more sensitive to both the molality m_j and the salt than is $G_m{}^E$. For dilute salt solutions $G_m{}^E < 0$ as a consequence of charge-charge interactions between the ions leading to a stabilisation. Further $H_m{}^E$ and $T.S_m{}^E$ are more sensitive to switching the solvent from H_2O to D_2O than is $G_m{}^E$.

The dependence of $G_m{}^E$ on salt at fixed m_j shows that in addition to charge-charge interactions there are further interactions which are characteristic of the ions in a given salt. So the suggestion is that even in the absence of charge-charge interactions the properties of the solution would not be ideal by virtue of cosphere - cosphere interactions along the lines suggested by Gurney. But there are two types of solutes in a simple 1:1 salt solution so we must consider in the analysis of these properties at least g_{++}, g_{+-} and g_{--} pairwise ion-ion Gibbs energy interaction parameters. Consequently the analysis is not straightforward.

An interesting approach examines patterns in $\ln(\gamma_\pm)$ for a series of 1:1 salts at fixed molality m_j, temperature and pressure [2-4]. A most dramatic change is observed for Pr_4N^+ salts (aq; $0.2\ molkg^{-1}$). Thus $\ln(\gamma_\pm) > (\ln \gamma_\pm(DHLL-\ calc\ ))$ for the fluoride salt ; i.e. a higher chemical potential than calculated simply on the basis of the DHLL-- a destabilisation. But $\ln(\gamma_\pm) > (\ln \gamma_\pm(DHLL-\ calc\ ))$ for the corresponding iodide salt; i.e. lower chemical potential than calculated simply on the grounds of the DHLL--- a stabilisation. The dependence of $\ln \gamma_\pm$ for K^+, Rb^+ and Cs^+ on the anion F^-, Cl^-, Br^- and I^- is much more modest. The pattern signals the important role of hydrophobic-hydrophobic, hydrophilic-hydrophobic and hydrophilic-hydrophilic ion-ion interactions. Indeed there is considerable merit in the approach [4]. The pattern emerges in a comparison of salt effects on rates of hydrolysis in aqueous salt solutions [5]. This conclusion is supported by the observation that the dependence of $\ln \gamma_\pm$ on $(m_j)^{1/2}$ for $(HOCH_2CH_2)_4\ N^+Br^-$ deviates from the DHLL pattern in a direction indicating a more hydrophilic character for the cation than in the cases of Pr_4N^+ and Et_4N^+ [6].

The patterns identified in $\ln \gamma_\pm$ signal that the ion-ion pair potential for ions in solution comprises several components. This recognition forms the basis of the treatment developed by Friedman and coworkers. The pair potential u_{ij} for two ions charge $z_i.e$ and $z_j.e$ in a solvent having relative permittivity ε_r is expressed in the form shown in equation (d) [6].

$$u_{ij}(r) = \left[\frac{(z_i\,e)\ (z_j\,e)}{4\,\pi\,\varepsilon_0\,\varepsilon_r\,r}\right] + COR_{ij} + CAV_{ij} + GUR_{ij}$$

The first term takes account of charge-charge interactions; i.e. the Coulombic term, COUL. The term COR_{ij} is a repulsive core potential , being a function of the sizes of the ions i and j. The CAV_{ij} term takes account of a special effect arising from the interactions between ion + solvent cavities. The impact of cosphere overlap is taken into account by the Gurney potential, GUR_{ij}. The pair potential is used in conjunction with McMillan-Mayer theory [8]. The Missing open brace for subscript term includes an adjustable parameter A_{ij}, the change in Helmholtz energy, F when one mole of solvent in the overlap region returns to the bulk solvent. There are therefore three such terms, A_{++}, A_{+-}, and A_{--} for the three types of overlap. These terms are related to the corresponding volumetric V_{ij}, entropy S_{ij} and energy U_{ij} terms. The analysis is slightly complicated by the fact that the derived thermodynamic functions refer to a solution in osmotic equilibrium with the solvent at the standard pressure; the MM state. Conversion is required to thermodynamic parameters for a solution of the same salt at the same molality at the standard pressure.

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1.10.26: Gibbs Energies- Binary Liquid Mixtures

Interest in the thermodynamic properties of binary liquid mixtures extended over most of the 19th Century. Interest was concerned with the vapour pressures of the components of a given binary mixture. Experimental work led Raoult to propose a law of partial vapour pressures which characterises a liquid mixture whose thermodynamic properties are ideal.

If liquid 1 is a component of a binary liquid mixture, components liquid 1 and liquid 2, the mixture is defined as having ideal thermodynamic properties if the partial vapour pressure at equilibrium $\mathrm{p_1(mix)}$ is related to the mole fraction composition using equation (a).

\[) p (mix) x p (* 1 1 1 = · l (a)

Here $\mathrm{p_1^*}(\ell)$ is the vapour pressure of pure liquid 1 at the same temperature. A similar equation describes the vapour pressure of liquid 2, $\mathrm{p_2(mix)}$ in the mixture. Raoult's Law as given in equation (a) forms the basis for examining the properties of real binary liquid mixtures.

Binary liquid mixtures [1-13] are interesting in their own right. Nevertheless chemists also use binary liquid mixtures as solvents for chemical equilibria and for media in which to carry out chemical reactions between solutes. In fact an enormous amount of our understanding of the mechanisms of inorganic and organic reactions is based on kinetic data describing the rates of chemical reactions in 80/20 ethanol and water mixtures. Because so much experimental information in the literature concerns the properties of solutes in binary aqueous mixtures we concentrate our attention on these systems. Indeed the properties of such solvent systems cannot be ignored when considering the properties of solutes in these mixtures. In examining the properties of binary aqueous mixtures we adopt a convention in which liquid water is chemical substance 1 and the non-aqueous liquid component is chemical substance 2. For the most part we describe the composition of a given liquid mixture (at defined temperature and pressure) using the mole fraction scale. Then if $\mathrm{n_1}$ and $\mathrm{n_2}$ are the amounts of chemical substances 1 and 2, the mole fractions are defined by equation (b) [12,13].

$$\mathrm{x_1 = n_1/(n_1 + n_2)} \quad \mathrm{x_2 = n_2/(n_1 + n_2)}$$

The chemical potentials of each component in a given liquid mixture, mole fraction composition $\mathrm{x_2 (= 1 - x_1)}$ are compared with the chemical potential of the pure liquid chemical potential at the same temperature and pressure, $\mu_1^*(\ell)$ and $\mu_2^*(\ell)$.

The starting point is a description of the equilibrium at temperature T between pure liquid and its saturated vapour in a closed system; i.e. a two phase system. [In terms of the Gibbs phase rule the number of components = 1; the number of phases = 2. Hence the number of degrees of freedom = 1. Then at a specified temperature the vapour pressure is defined.] The equilibrium is described in terms of the equality of chemical potentials of substance 1 in the two phases; equation (c).

$$\mu_1 (\ \mathrm{g; p_1^*; T}) = \mu_1 (\ell; \mathrm{p_1^*; T})$$

Thus $\mu_1 (\ell; \mathrm{p_1^*; T})$ is the molar Gibbs energy of the pure liquid 1, otherwise the chemical potential.

However our interest concerns the properties of binary liquid mixtures. Using the Gibbs phase rule, number of phases = 2; number of components = 2; hence number of degrees of freedom = 2. Then for a defined temperature and mole fraction composition the vapour pressure $\mathrm{p(mix)}$ is fixed. Equation (d) describes the equilibrium between liquid and vapour phases with reference to liquid substance 1.

$$\mu_1 (\ \mathrm{g; p_1; T}) = \mu_1 (\mathrm{mix; x_1; p; T})$$

Equations (c) and (d) offer a basis for comparing the chemical potentials of chemical substance 1 in the two phases, liquid and vapour.

$$\mu_1 (\ \mathrm{g; p_1^*; T}) - \mu_1 (\ \mathrm{g; p_1; T}) = \mu_1 (\ell; \mathrm{p_1^*; T}) - \mu_1 (\mathrm{mix; x_1; p; T})$$

Analysis of vapour pressure data is not straightforward because account has to be taken of the fact that the properties of real gases are not those of an ideal gas. However here we assume that the properties of chemical substance in the gas phase are ideal. Consequently we use the following equation to provide an equation for the r.h.s. of equation (e) in terms of two vapour pressures.

$$\mu_1 (\mathrm{mix; x_1; p; T}) = \mu_1 (\ell; \mathrm{p_1^*; T}) + \mathrm{R\,T\ ln\,(p_1/p_1^*)}$$

Equation (a) is combined with equation (f) to yield the following equation for chemical substance 1 as component of the binary liquid mixture.

$$\mu_1\,(\mathrm{mix;id;x_1}) = \mu_1^*(\ell) + \mathrm{R\,T\,\ln\,(x_1)}$$

Similarly for chemical substance 2 in the liquid mixture,

$$\mu_2\,(\mathrm{mix;id;x_2}) = \mu_2^*(\ell) + \mathrm{R\,T\,\ln\,(x_2)}$$

Hence for an ideal binary liquid mixture, formed by mixing $\mathrm{n_1}$ and $\mathrm{n_2}$ moles respectively of chemical substance 1 and 2, the Gibbs energy of the mixture is given by equation (i).

$$\mathrm{G(mix;id)} = \\ \mathrm{n_1}\,[\mu_1^*(\ell) + \mathrm{R\,T\,\ln\,(x_1)}] + \mathrm{n_2}\,[\mu_2^*(\ell) + \mathrm{R\,T\,\ln\,(x_2)}]$$

Bearing in mind that Gibbs energies cannot be measured for either a pure liquid or a liquid mixture, it is useful to rephrase equation (i) in terms of the change in Gibbs energy that accompanies mixing to form an ideal binary liquid mixture. We envisage a situation where before mixing the molar Gibbs energy of the system defined as $\mathrm{G(no-mix)}$ is given by equation (j).

$$\mathrm{G(no-mix)} = \mathrm{n_1}\,\mu_1^*(\ell) + \mathrm{n_2}\,\mu_2^*(\ell)$$

The change in Gibbs energy on forming the ideal binary liquid mixture $\Delta_{\mathrm{mix}}\mathrm{G}$ is given by the equation (k).

$$\Delta_{\mathrm{mix}}\,\mathrm{G(id)} = \mathrm{R\,T}\,[\mathrm{n_1}\,\ln\,(\mathrm{x_1}) + \mathrm{n_2}\,\ln\,(\mathrm{x_2})]$$

We re-express $\Delta_{\mathrm{mix}}\mathrm{G}$ in terms of the Gibbs energy of mixing forming one mole of the ideal binary liquid mixture.

$$\Delta_{\mathrm{mix}}\,\mathrm{G_m} = \Delta_{\mathrm{mix}}\,\mathrm{G}/\,(\mathrm{n_1} + \mathrm{n_2})$$

Hence,

$$\Delta_{\mathrm{mix}}\,\mathrm{G_m(id)} = \mathrm{R\,T}\,[\mathrm{x_1}\,\ln\,(\mathrm{x_1}) + \mathrm{x_2}\,\ln\,(\mathrm{x_2})]$$

As required,

$$\mathrm{limit}\,(\mathrm{x_1} \to 0)\,\Delta_{\mathrm{mix}}\mathrm{G_m(id)} = 0$$

$$\mathrm{limit}\,(x_2 \to 0)\,\Delta_{\mathrm{mix}}\,G_m(\,\mathrm{id}\,) = 0$$

The dependence of $\Delta_{\mathrm{mix}}\mathrm{G_m(id)/R\,T}$ on mole fraction composition is defined by equation (m). For a mixture where $x_1 = x_2 = 0.5$,

$$\Delta_{\mathrm{mix}}\,\mathrm{G_m(id)/R\,T} = 2.0 \times 0.5 \times \ln(0.5) = -0.693$$

In fact the molar Gibbs energy of mixing for an ideal binary liquid mixture is negative across the whole composition range.

Equation (m) is the starting point of most equations used in the analysis of the properties of binary liquid mixtures. In fact most of the chemical literature concerned with liquid mixtures describes the properties of aqueous mixtures, at ambient pressure and $298.15\ \mathrm{K}$. Nevertheless an extremely important subject concerns the properties of liquid mixtures at high pressures [14,15].

Footnotes

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[12] According to Phase Rule, P = 2 (for liquid and vapour), C = 2 then F = 2 + 2 - 2 = 2. Having defined temperature and pressure there remain no degrees of freedom - the system is completely specified.

[13] Other methods of defining the composition include the following.

Mass % [or w%] Mass of component $1 = \mathrm{n_1\,M_1}$ Mass of component $2 = \mathrm{n_2\,M_2}$

Then

$$\mathrm{w_1\% = \frac{n_1\,M_1\,100}{[n_1\,M_1 + n_2\,M_2]}} \quad \mathrm{w_2\% = 100 - w_1\%}$$

Volume % This definition often starts out by defining the volumes of the two liquid components used to prepare a given mixture at defined temperature and pressure. The definition does not normally refer to the volume of the actual mixture. The volume after mixing is often less than the sum of the component volumes before mixing.

$$\mathrm{V_1^*(\ell) = n_1\,M_1/\rho_1^*(\ell)} \quad \mathrm{V_2^*(\ell) = n_2\,M_2/\rho_2^*(\ell)}$$
$$\mathrm{V_2\% = \frac{V_2^*(\ell)}{V_1^*(\ell) + V_2^*(\ell)}}$$

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1.10.27: Gibbs Energies- Binary Liquid Mixtures- General Properties

A given binary liquid mixture (at temperature T and pressure p, which is close to the standard pressure) mole fraction $x_1 (= 1 - x_2)$ can be characterised by the molar Gibbs energy of mixing, $\Delta_{mix}\ G_m$ and related molar enthalpic, volumetric and entropic properties. A corresponding set of properties exists for this mixture granted that the thermodynamic properties are ideal; e.g. $\Delta_{mix}\ G_m(\mathrm{id})$. Hence we can define the corresponding excess molar property, $G_m^E = \Delta_{mix}G_m - \Delta_{mix}G_m\ (\mathrm{id})$. Interesting patterns emerge relating these properties and the corresponding partial molar properties; e.g. chemical potentials.

Ideal Mixing Properties

At defined T and p, the molar Gibbs energy for an ideal binary liquid mixture is given by equation (a).

$$G_m(\mathrm{id}) = x_1\ [\mu_1^*(\ell) + R\,T\ \ln(x_1)] + x_2\ [\mu_2^*(\ell) + R\,T\ \ln(x_2)]$$

Here $\mu_1^*(\ell)$ and $\mu_2^*(\ell)$ are the chemical potentials of the two pure liquids 1 and 2 at the same T and p. If the same amounts of the two liquid had not been allowed to mix,

$$G_m(\ \mathrm{no}\ -\mathrm{mix}) = x_1\,\mu_1^*(\ell) + x_2\,\mu_2^*(\ell)$$

By definition,

$$\Delta_{mix}\ G_m(\mathrm{id}) = x_1\,R\,T\ \ln(x_1) + x_2\,R\,T\ \ln(x_2)$$

Recalling that $x_1 + x_2 = 1$ and $dx_1 = -dx_2$,

$$d\Delta_{mix}\ G_m(\mathrm{id})/dx x_2 = -R\,T\ \ln(x_1) - R\,T + R\,T\ \ln(x_2) + R\,T$$

We use equation (c) for $\ln(x_2)$ and substitute in equation (d).

$$d\Delta_{mix}\ G_m(\mathrm{id})/dx x_2 = \\ -R\,T\ \ln(x_1) + (1/x_2)\ [\Delta_{mix}\ G_m(\mathrm{id}) - x_1\,R\,T\ \ln(x_1)]$$

$$x_2\,d\Delta_{mix}G_m(\mathrm{id})/dx x_2 = \\ -x_2\,R\,T\ \ln(x_1) + \Delta_{mix}\ G_m(\mathrm{id}) - x_1\,R\,T\ \ln(x_1)]$$

Hence,

$$R\,T\ \ln(x_1) = \Delta_{mix}G_m(\mathrm{id}) - x_2\,d\Delta_{mix}G_m(\mathrm{id})/dx x_2$$

At all mole fractions, $\Delta_{mix}G_m(\mathrm{id})$ is negative, the plot of $\Delta_{mix}G_m(\mathrm{id})$ against x_1 being symmetric about '$x_1 = 0.5$'. At the extreme, where $d\Delta_{mix}G_m(\mathrm{id})/dx x_2$ is zero; equation (c) shows that $\Delta_{mix}G_m(\mathrm{id})$ equals $[R\ T\ \ln(0.5)]$. At 298 K, the latter quantity equals –1.72 kJmol^{-1}.

Using equation (c), the ratio $\Delta_{mix}G_m(\mathrm{id})/T$ is given by equation (h)

$$\Delta_{mix}G_m(\mathrm{id})/T = R\ [x_1\ \ln(x_1) + x_2\ \ln(x_2)]$$

Hence using the Gibbs-Helmholtz it follows that the molar enthalpy of mixing is zero at all mole fractions. Similarly the molar isobaric heat capacity of mixing is zero at all mole fractions. In terms of entropies,

$$\Delta_{mix}S_m(\mathrm{id}) = -R\ [x_1\ \ln(x_1) + x_2\ \ln(x_2)]$$

But at all (real) mole fractions (other than $x_1 = 1$ and $x_2 = 1$) $[x_1\ \ln(x_1) + x_2\ \ln(x_2)] < 0$. Hence $\Delta_{mix}S_m(\mathrm{id}) > 0$. In the event that mixing of two liquids at temperature T to produce a binary liquid mixture having ideal properties, then $\Delta_{mix}\ G_m(\mathrm{id})$ is negative because $\Delta_{mix}S_m(\mathrm{id})$ is positive, $\Delta_{mix}\ H_m(\mathrm{id})$ being zero. In other words we have a reference against which to examine the properties of real liquid mixtures.

Excess properties

The molar Gibbs energy of a real binary liquid mixture is related to the mole fraction composition using equation (j).

$$G_m = \\ x_1\ [\mu_1^*(\ell) + R\,T\ \ln(x_1\,f_1)] + x_2\ [\mu_2^*(\ell) + R\,T\ \ln(x_2\,f_2)]$$

For the corresponding mixture having ideal thermodynamic properties,

$$\mathrm{G_m(id)} = \\ \mathrm{x_1}\ [\mu_1^*(\ell) + \mathrm{R\,T\ ln\,(x_1)}] + \mathrm{x_2}\ [\mu_2^*(\ell) + \mathrm{R\,T\ ln\,(x_2)}]$$

The excess molar Gibbs energy $\mathrm{G_m}^{\mathrm{E}}$ is therefore given by equation (l).

$$\mathrm{G_m^E = R\,T\ [x_1\ ln\,(f_1) + x_2\ ln\,(f_2)]}$$

We differentiate equation (l) with respect to mole fraction, x_1.

$$\frac{1}{RT}\frac{\mathrm{dG_m^E}}{\mathrm{dx_1}} = \mathrm{ln\,(f_1)} + \mathrm{x_1}\frac{\mathrm{d\,ln\,(f_1)}}{d\mathrm{x_1}} - \mathrm{ln\,(f_2)} + \mathrm{x_2}\frac{\mathrm{d\,ln\,(f_2)}}{\mathrm{dx_1}}$$

But from the Gibbs-Duhem equation at fixed T and p,

$$x_1\frac{d\,\mathrm{ln}\,(\mu_1)}{dx_1} + x_2\frac{d\,\mathrm{ln}\,(\mu_2)}{dx_1} = 0$$

Hence,

$$x_1\frac{d\,\mathrm{ln}\,(f_1)}{dx_1} + x_2\frac{d\,\mathrm{ln}\,(f_2)}{dx_1} = 0$$

From equation (k),

$$\mathrm{ln}\,(f_2) = \mathrm{ln}\,(f_1) - \frac{1}{RT}\frac{dG_m^E}{dx_1}$$

Hence using equation (j),

$$\frac{\mathrm{G_m^E}}{\mathrm{R\,T}} = \mathrm{ln\,(f_1)} - \frac{\mathrm{X_2}}{\mathrm{R\,T}}\frac{\mathrm{dG_m^E}}{\mathrm{dx}}$$

Or

$$\mathrm{ln\,(f_1)} = \frac{\mathrm{G_m^E}}{\mathrm{R\,T}} = +\frac{\mathrm{x_2}}{\mathrm{R\,T}}\frac{\mathrm{dG_m^E}}{\mathrm{dx_1}}$$

Equation (o) has an interesting feature. At the mole fraction composition where $\frac{\mathrm{dG_m^E}}{\mathrm{dx_1}}$ is zero, $\frac{\mathrm{G_m^E}}{\mathrm{R\,T}}$ offers a direct measure of $\mathrm{ln}\,(f_1)$ at that mole fraction.

Perhaps the most direct measure of the extent to which the thermodynamic properties of a given binary liquid mixture differs from that defined as ideal is afforded by the molar enthalpy of mixing which is therefore the excess molar enthalpy of mixing \({\mathrm{H}_{\mathrm{m}}}^{\mathrm{E}}\). Thus,

$$\mathrm{G_m^E = H_m^E - T\,S_m^E}$$

where

$$\mathrm{C_{pmn}^E} = \left(\partial \mathrm{H_m^E}/\partial \mathrm{T}\right)_{\mathrm{p}}$$

In many reports the properties of a given binary liquid mixture at 298.15 K and ambient pressure are summarised in a plot showing the three properties \({\mathrm{G}_{\mathrm{m}}}^{\mathrm{E}}\), \({\mathrm{H}_{\mathrm{m}}}^{\mathrm{E}}\) and $\mathrm{T\ S_m^E}$ as a function of the mole fraction composition. An enormous amount of information can be summarised in such plots. In order to understand the various patterns which emerge two liquid mixtures are often taken as models against which to compare the properties of other liquid mixtures.

i. Trichloromethane + Methanol
   For this mixture both \({\mathrm{G}_{\mathrm{m}}}^{\mathrm{E}}\) and \({\mathrm{H}_{\mathrm{m}}}^{\mathrm{E}}\) are negative, their minima being at approx. mole fractions at 0.5. The pattern in understood in terms of strong inter-component interaction, hydrogen bonding. In these terms the mixing is ‘favourable’ and exothermic.

ii. Tetrachloromethane + Methanol

For this mixture the mixing is, for the most part endothermic and \({\mathrm{G}_{\mathrm{m}}}^{\mathrm{E}}\) is positive with a maximum at mole fractions equal to 0.5. Thus the mixing is unfavourable and endothermic. This pattern points to the impact of added tetrachloromethane disrupting the intermolecular hydrogen bonding between methanol molecules.

These two liquid mixtures provide a basis for the examination of the properties of binary aqueous mixtures for which there is an immense published information. In most cases \({\mathrm{G}_{\mathrm{m}}}^{\mathrm{E}}\) is either positive or negative across the mole fraction range for a given liquid mixture although plots of \({\mathrm{G}_{\mathrm{m}}}^{\mathrm{E}}\) and $T S_m^E$ against mole fraction composition are often S-shaped, nevertheless operating to produce a smooth change in \({\mathrm{G}_{\mathrm{m}}}^{\mathrm{E}}\). Plots of ${C_{pm}}^E$ and excess molar volume of mixing ${V_m}^E$ against mole fraction are often quite complicated.

In a few cases the plot of \({\mathrm{G}_{\mathrm{m}}}^{\mathrm{E}}\) against composition is S-shaped. One such system is the mixture, water + 1,1,1,3,3,3-hexafluoropropanol [1]. Explanations of such complex patterns are not straightforward. However we might for an alcohol + water mixture envisage a switch from

i. at low x_2 strong water-water interactions with weak alcohol-water interactions to
ii. at high x_2 strong alcohol-water interactions.

Definition of excess thermodynamic properties is not straightforward in all instances; e.g. isentropic compressibilities.[2]

Footnotes

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1.10.28: Gibbs Energies- Liquid Mixtures- Thermodynamic Patterns

A given binary liquid mixture (at temperature T and pressure p, which is close to the standard pressure) mole fraction $x_1 \, (= 1 - x_2)$ is characterised by the molar Gibbs energy of mixing, $\Delta_{\mathrm{mix}}\mathrm{G_m}$ and related molar enthalpic, volumetric and entropic properties. A corresponding set of properties for this mixture exist granted that the thermodynamic properties are ideal; e.g. $\Delta_{\mathrm{mix}}\mathrm{G_m(id)}$. As a consequence we define the corresponding excess molar property, $\mathrm{G_m^E} = \Delta_{\mathrm{mix}}\mathrm{G_m} - \Delta_{\mathrm{mix}}\mathrm{G_m}\ (\mathrm{id})$. Interesting patterns emerge relating these properties and the corresponding partial molar properties; e.g. chemical potentials.

For chemical substance 1, (which we will conventionally take as water) the chemical potential in the liquid mixture is related to the chemical potential of the pure liquid at the same T and using equation (a) where x_1 is the mole fraction and $\mathrm{f_1}$ is the rational activity coefficient.

$$\mu_1(\mathrm{mix}) = \mu_1^*(\ell) + \mathrm{R\,T\ ln\,(x_1\,f_1)}$$

where

$$\mathrm{limit\,(x_1 \rightarrow 1)\,f_1 = 1.0\ at\ all\ T\ and}\ p$$

Similarly for component 2,

$$\mu_2(\mathrm{mix}) = \mu_2^*(\ell) + \mathrm{R\,T\ ln\,(x_2\,f_2)}$$

where

$$\mathrm{limit\,(x_2 \rightarrow 1)\,f_2 = 1.0\ at\ all\ T\ and\ p}$$

Here $\mu_1^*(\ell)$ and $\mu_2^*(\ell)$ are the chemical potentials of the two pure liquids at the same T and p; $\mathrm{f_1}$ and $\mathrm{f_2}$ are rational activity coefficients. These (rational) activity coefficients approach unity at opposite ends of the mixture composition range. For the aqueous component, as x_1 approaches 1, so $\mathrm{f_1}$ approaches unity (at the same T and p). At the other end of the scale, as x_1 approaches zero so the chemical potential of water in the binary system approaches ‘minus infinity’. If across the whole composition range (at all T and p), both $\mathrm{f_1}$ and $\mathrm{f_2}$ are unity, the thermodynamic properties of the liquid mixture are ideal.

A given liquid mixture (at fixed T and p) is formed by mixing $\mathrm{n_1}$ moles of liquid 1 and $\mathrm{n_2}$ moles of liquid 2. Before mixing the total Gibbs energy of the system, defined as G(no-mix) is given by the following equation where $\mu_1^*(\ell)$ and $\mu_2^*(\ell)$ are the chemical potentials of the two pure liquids at the same T and p. Then,

$$\mathrm{G(no-mix) = n_1\,\mu_1^*(\ell) + n_2\,\mu_2^*(\ell)}$$

After mixing, the Gibbs energy of the mixture is given by equation (f).

$$\mathrm{G(mix) = \\ n_1\ [\mu_1^*(\ell) + R\,T\ ln\,(x_1\,f_1)] + n_2\ [\mu_2^*(\ell) + R\,T\ ln\,(x_2\,f_2)]}$$

By definition,

$$\Delta_{\mathrm{mix}}\mathrm{G} = \mathrm{G(mix)} - \mathrm{G(no-mix)}$$

Hence the Gibbs energy of mixing ,

$$\Delta_{\mathrm{mix}}\ \mathrm{G} = \mathrm{R\,T\ [n_1\ ln\,(x_1\,f_1)] + [n_2\ ln\,(x_2\,f_2)]}$$

We re-express $\Delta_{\mathrm{mix}}\mathrm{G}$ in terms of the Gibbs energy of mixing for one mole of liquid mixture. Thus

$$\Delta_{\mathrm{mix}}\ \mathrm{G_m} = \Delta_{\mathrm{mix}}\ \mathrm{G/\,(n_1 + n_2)}$$

Hence,

$$\Delta_{\mathrm{mix}}\mathrm{G_m} = \mathrm{R\,T\ [x_1\ ln\,(x_1\,f_1) + x_2\ ln\,(x_2\,f_2)]}$$

Or,

\[\Delta_{\text {mix }} G_{m}=R \, T \,\left[x_{1} \, \ln \left(x_{1}\right)+x_{1} \, \ln \left(f_{1}\right)+x_{2} \, \ln \left(x_{2}\right)+x_{2} \, \ln \left(f_{2}\right)\right]]

By definition,

$$\Delta_{\text{mix}}\,\mathrm{G_m(id)} = \mathrm{x_1\,R\,T\,\ln(x_1) + x_2\,R\,T\,\ln(x_2)}$$

Recalling that $x_1 + x_2 = 1$ and $dx_1 = -dx_2$,

$$\mathrm{d\Delta_{mix}G_m(id)/dxx_2 = -R\,T\,\ln(x_1) - R\,T + R\,T\,\ln(x_2) + R\,T}$$

We use equation (l) for $\ln(\mathrm{x_2})$ and substitute in equation (m).

$$\mathrm{d\Delta_{mix}\,G_m(id)/dxx_2 =}$$
$$\mathrm{-\,R\,T\,\ln(x_1) + (1/x_2)\,[\Delta_{mix}\,G_m(id) - x_1\,R\,T\,\ln(x_1)]}$$

or,

$$x_2\,d\Delta_{\text{mix}}\,G_m(\text{id})/dx_2 =$$
$$-x_2\,RT\,\ln(x_1) + \Delta_{\text{mix}}\,G_m\ (\text{id})\ - x_1\,RT\,\ln(x_1)]$$

Hence,

$$\mathrm{R\,T\,\ln(x_1) = \Delta_{mix}G_m(id) - x_2\,d\Delta_{mix}G_m(id)/dxx_2}$$

At all mole fractions, $\Delta_{\text{mix}}G_m(\ \text{id}\ )$ is negative; the plot of $\Delta_{\text{mix}}\,G_m\ (\text{id})$ against x_1 is symmetric about '$x_1 = 0.5$'. At the extremum, where $\mathrm{d\Delta_{mix}G_m(id)/dxx_2}$ is zero, equation (l) shows that $\Delta_{\text{mix}}\mathrm{G_m(id)}$ equals $\mathrm{R\,T\,ln(0.5)}$.

We define an excess chemical potential for each of the two components of a binary liquid mixture. For liquid component 1,

$$\mu_1^{\mathrm{E}}(\text{mix}) = \mu_1(\text{mix}) - \mu_1^*(\ell) - \mathrm{R\,T\,\ln(x_1) = R\,T\,\ln(f_1)}$$

Similarly for liquid component 2,

$$\mu_2^{\mathrm{E}}(\text{mix}) = \mu_2(\text{mix}) - \mu_2^*(\ell) - \mathrm{R\,T\,\ln(x_2) = R\,T\,\ln(f_2)}$$

Rational activity coefficients $\mathrm{f_1}$ and $\mathrm{f_2}$ depend on mixture composition, T and p.

In summary 'excess' means excess over ideal. Excess properties provide a mutually consistent set of perspectives of a given liquid mixture. We define a reference state for binary liquid mixtures so that the thermodynamic properties of a given liquid mixture can be correlated with a common model.

A convenient approach defines an excess molar Gibbs energy of mixing.

$$\mathrm{G_m^E = \Delta_{mix}G_m - \Delta_{mix}G_m\ (id)}$$

Then

$$\mathrm{G_m^E = R\,T\,[x_1\,\ln(f_1) + x_2\,\ln(f_2)]}$$

Where

$$\mathrm{limit\,(x_1 \to 1)\,G_m^E = 0}$$

And

$$\mathrm{limit\,(x_2 \to 1)\,G_m^E = 0}$$

Other than the latter two conditions we cannot predict the dependence of $\mathrm{G_m{}^E}$ on a mixture composition for m a given real mixture. [1]

In general terms excess molar properties of binary aqueous mixtures are expressed in terms of the following general equation with respect to the thermodynamic variable $\mathrm{Q(=\ G,\ V,\ H\ and\ S)}$.

$$\mathrm{Q_m^E = Q_m(\ mix\ ) - Q_m(\ mix\ ;\ ideal\ )}$$

Returning to the Gibbs energies, we differentiate equation (t) with respect to mole fraction x_1 at fixed T and p.

$$\frac{1}{RT}\,\frac{dG_m^E}{dx_1} = \ln(f_1) + x_1\,\frac{d\ln(f_1)}{dx_1} - \ln(f_2) + x_2\,\frac{d\ln(f_2)}{dx_1}$$

According to the Gibbs-Duhem equation, at fixed T and p,

$$\mathrm{x_1}\,\frac{\mathrm{d}\ln(\mu_1)}{\mathrm{dx_1}} + \mathrm{x_2}\,\frac{\mathrm{d}\ln(\mu_2)}{\mathrm{dx}} = 0$$

Hence,

$$x_1\,\frac{d\ln(f_1)}{dx_1} + x_2\,\frac{d\ln(f_2)}{dx_1} = 0$$

From equation (x),

$$\ln(f_2) = \ln(f_1) - \frac{1}{RT}\,\frac{dG_m^E}{dx_1}$$

Hence using equation (t),

$$\frac{\mathrm{G_m^E}}{\mathrm{R\,T}} = \ln(\mathrm{f_1}) - \frac{\mathrm{x_2}}{\mathrm{R\,T}}\,\frac{\mathrm{dG_m^E}}{\mathrm{dx_1}}$$

Or

$$\ln(f_1) = \frac{G_m^E}{RT} + \frac{x_2}{RT}\,\frac{dG_m^E}{dx_1}$$

Equation (zc) has an interesting feature. At the mole fraction composition where $\frac{\mathrm{dG_m^E}}{\mathrm{dx_1}}$ is zero, $\frac{\mathrm{G_m^E}}{\mathrm{R\,T}}$ offers a direct measure of $\ln(\mathrm{f_1})$ at that mole fraction. In some systems the plot of $\mathrm{G_m{}^E}$ against composition is S-shaped so we have this information at two mole fractions.

Turning to volumetric properties, the molar volume of an ideal binary liquid mixture is given by equation (zd).

$$\mathrm{V_m} = \mathrm{x_1}\,\mathrm{V_1^*}(\ell) + \mathrm{x_2}\,\mathrm{V_2^*}(\ell)$$

Hence,

$$\mathrm{V_m^E} = \mathrm{x_1}\,[\mathrm{V_1(mix)} - \mathrm{V_1^*}(\ell)] + \mathrm{x_2}\,[\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)]$$

$$\frac{\mathrm{dV_m^E}}{\mathrm{dxx_1}} =$$

$$[\mathrm{V_1(mix)} - \mathrm{V_1^*}(\ell)] + \mathrm{x_1}\,\frac{\mathrm{dV_1}}{\mathrm{dx_1}} - [\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)] + \mathrm{x_2}\,\frac{\mathrm{dV_2}}{\mathrm{dx_1}}$$

Using the Gibbs-Duhem equation,

$$\frac{\mathrm{dV_m^E}}{\mathrm{dx_1}} = [\mathrm{V_1(mix)} - \mathrm{V_1^*}(\ell)] - [\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)]$$

or,

$$[\mathrm{V_1(mix)} - \mathrm{V_1^*}(\ell)] = \frac{\mathrm{dV_m^E}}{\mathrm{dxx_1}} + [\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)]$$

$$\mathrm{V_m^E} = \mathrm{x_1}\,\frac{\mathrm{dV_m^E}}{\mathrm{dxx_1}} + \mathrm{x_1}\,[\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)] + \mathrm{x_2}\,[\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)]$$

Hence,

$$[\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)] = \mathrm{V_m^E} - \mathrm{x_1}\,\frac{\mathrm{dV_m^E}}{\mathrm{dxx_1}}$$

At the composition where $\mathrm{dV_m^E/dx_1}$ is zero, $[\mathrm{V_2(mix)} - \mathrm{V_2^*}(\ell)] = \mathrm{V_m^E}$.

The analysis set out above is repeated for excess molar enthalpies and excess molar isobaric heat capacities for binary liquid mixtures.

Interesting proposals have been made in which the dependence of excess thermodynamic properties on mixture composition are examined in different composition domains; e.g. the four segment model [2-9].

Footnotes

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1.10.29: Gibbs Energies- Binary Liquid Mixtures- Excess Thermodynamic Variables

The properties of binary mixtures are complicated. As a point of reference the excess molar properties of two non-aqueous binary liquid mixtures are often discussed. The mixtures are (A) trichloromethane + propanone, and (B) tetrachloromethane + methanol.

A snapshot of the thermodynamic properties of a given binary mixture (at fixed T and p) is provided by combined plots of $\mathrm{G_m}^{\mathrm{E}}$, $\mathrm{H_m}^{\mathrm{E}}$ and $\mathrm{T\,S_m^E}$ as a function of mixture composition [1-5]. In effect the starting point is the Gibbs energy leading to first, second, third and fourth derivatives [6]. At this stage we make some sweeping (and dangerous) generalizations. For most binary aqueous mixtures, $\mathrm{G_m}^{\mathrm{E}}$ is a smooth function of water m mole fraction x_1, with an extremum near $x_1 = 0.5$. Rarely for a given mixture does the sign of $\mathrm{G_m}^{\mathrm{E}}$ change across the mole faction range m although this feature is not unknown; e.g. water + 1,1,1,3,3,3-hexafluropropan-2-ol mixtures at $298.15\ \mathrm{K}$ [7] but contrast water + 2,2,2- trifluorethanol mixtures [8] where at $298.2\ \mathrm{K}$ $\mathrm{G_m}^{\mathrm{E}}$ is positive across the m whole mole fraction range. However a change in sign of $\mathrm{H_m}^{\mathrm{E}}$ and $\mathrm{T\ S_m}^{\mathrm{E}}$ and $\mathrm{V_m}^{\mathrm{E}}$ with change in mole fraction composition is quite common.

For mixture A, $\mathrm{G_m}^{\mathrm{E}}$ is negative indicating that $\Delta_{\mathrm{mix}}\mathrm{G_m}$ is more negative than in the case of an ideal binary liquid mixture. In the case of Mixture A, the negative $\mathrm{G_m}^{\mathrm{E}}$ is linked with a marked exothermic mixing; $\mathrm{H_m}^{\mathrm{E}} < 0$. The latter is attributed to strong inter-component hydrogen bonding.

For both mixtures A and B the signs of $\mathrm{G_m}^{\mathrm{E}}$ and $\mathrm{H_m}^{\mathrm{E}}$ are the same. This feature is characteristic of binary non-aqueous liquid mixtures where in most instances, $\left|\mathrm{H_m^E}\right| > \left|\mathrm{T\,S_{mm}^E}\right|$. $\mathrm{G_m}^{\mathrm{E}}$ and $\mathrm{H_m}^{\mathrm{E}}$ are both positive for mixture B. Here the pattern is understood in terms of disruption of methanol-methanol hydrogen bonding (i.e. intracomponent interaction) by the second component. Again we note that a positive $\mathrm{G_m}^{\mathrm{E}}$ means that the tendency for $\Delta_{\mathrm{mix}}\mathrm{G_m}$ to be negative (cf. ideal mixtures) is opposed.

Through a series of mixtures with increasing $\mathrm{G_m}^{\mathrm{E}}$, a stage is reached where the magnitude of $\mathrm{G_m}^{\mathrm{E}}$ is such that phase separation occurs [1]. For m many binary non-aqueous binary liquid mixtures the phase diagram for liquid miscibility has an upper critical solution temperature UCST. In other words only at high temperatures is the liquid mixture miscible in all proportions.

Often binary aqueous mixtures are used as solvents for the following reason. The solubilities of salts in water(l) are high because ‘water is a polar solvent’ but the solubilities of apolar solutes are low. However the solubilities of apolar substances in organic solvents (e.g. ethanol) are high. If the chemical reaction being studied involves both polar and apolar solutes, judicious choice of the composition of a binary aqueous mixture leads to a solvent where the solubilities of both polar and apolar solutes are high. Nevertheless the task of accounting for the properties of binary aqueous mixtures is awesome. For this reason the classification introduced by Franks [9] has considerable merit. A distinction is drawn between Typically Aqueous and Typically Non-Aqueous Binary Aqueous Mixtures, based on the the thermodynamic excess functions, $\mathrm{G_m}^{\mathrm{E}}$, $\mathrm{H_m}^{\mathrm{E}}$ and $\mathrm{T\,S_m}^{\mathrm{E}}$.

Davis has explored how the properties of many binary aqueous mixtures can be subdivided on the basis of the ranges of mole fraction compositions [10].

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1.10.30: Gibbs Energies- General Equations

For binary liquid mixtures at fixed T and p, an important task is to fit the dependence of ${\mathrm{G_m}}^{\mathrm{E}}$ on x_2 to an equation in order to calculate the derivative $\mathrm{dG_m^E/dx_2}$ at required mole fractions. The Guggenheim - Scatchard [1,2] (commonly called the Redlich - Kister [3]) equation is one such equation. This equation has the following general form.

$$\mathrm{X_m^E = x_2\ (1 - x_2)} \sum_{\mathrm{i=1}}^{\mathrm{i=k}} \mathrm{A_i\ (1 - 2\,x_2)^{i-1}}$$

$\mathrm{A_i}$ are coefficients obtained from a least squares analysis of the dependence of ${\mathrm{G_m}}^{\mathrm{E}}$ on x_2.The equation clearly satisfies the condition that ${\mathrm{G_m}}^{\mathrm{E}}$ is zero at $x_2 = 0$ and at $x_2 = 1$. In fact the first term in the $\mathrm{G - S}$ equation has the following form.

$$X_m^E = X_2\ (1 - X_2)\ A_1$$

According to equation (b) ${\mathrm{X_m}}^{\mathrm{E}}$ is an extremum at $x_2 = 0.5$, the plot being symmetric about the line from ${\mathrm{X_m}}^{\mathrm{E}}$ to '$x_2 = 0.5$'. In fact for most systems the $\mathrm{A_1}$ term is dominant. For the derivative $\mathrm{dG_m^E/dxx_2}$, we write equation (a) in the following general form.

$$\mathrm{X_m^E = \left(x_2 - x_2^2\right)\ Q}$$

Then

$$\mathrm{dX_m^E/dxx_2 = x_2\ (1 - x_2)\ dQ/dxx_2 + (1 - 2\,x_2)\ Q}$$

where

$$\mathrm{dQ/dx_2 = -2} \sum_{\mathrm{i=2}}^{\mathrm{i=k}} \mathrm{(i - 1)\,A_i\ (1 - 2\,x_2)^{i-2}}$$

Equation (a) fits the dependence with a set of contributing curves which all pass through points, ${\mathrm{X_m}}^{\mathrm{E}} = 0$ at $x_1 = 0$ and $x_1 = 1$. The usual procedure involves fitting the recorded dependence using increasing number of terms in the series, testing the statistical significance of including a further term. Although equation (a) has been applied to many systems and although the equation is easy to incorporate into computer programs using packaged least square and graphical routines, the equation suffers from the following disadvantage. As one incorporates a further term in the series, (e.g. A_j) estimates of all the previously calculated parameters (i.e. $\mathrm{A_2,\ A_{3...}\ ...\ A_{j-1}}$) change. For this reason orthogonal polynomials have been increasingly favoured especially where the appropriate computer software is available. The only slight reservation is that derivation of explicit equations for the required derivative ${\mathrm{dX_m}}^{\mathrm{E}}$ is not straightforward. The problem becomes rather more formidable when the second and higher derivatives are required. The derivative ${\mathrm{d^2X_m}}^{\mathrm{E}}$ is sometimes required by calculations concerning the properties of binary liquid mixtures.

The derivative $\mathrm{dG_m^E/dxx_1}$ and ${\mathrm{G_m}}^{\mathrm{E}}$ are combined to yield an equation for $\mathrm{ln\,(f_1)}$.

$$\ln\left(f_1\right) = \frac{G_m^E}{RT} + \frac{(1 - x_1)}{RT}\,\frac{dG_m^E}{dx_1}$$

A similar equation leads to estimates of $\mathrm{ln\,(f_2)}$. Hence the dependences are obtained of both $\mathrm{ln\,(f_1)}$ and $\mathrm{ln\,(f_2)}$ on mixture composition. It is of interest to explore the case where the coefficients $\mathrm{A_2,\ A_3}$ ... in equation (a) are zero. Then

$$\mathrm{X_m^E = x_2\ (1 - x_2)\ A_1}$$

and

$$\mathrm{dX_m^E/dx_2 = (1 - 2\,X_2)\ A_1}$$

With reference to the Gibbs energies,

$$\mathrm{ln\,(f_2) = (1/R\,T)\ [x_2\ (1 - x_2) + (1 - x_2)\ (1 - 2\,x_2)]\ A_1^G}$$

$$\mathrm{ln\,(f_2) = \left(A_1^G/R\,T\right)\ \left[1 - 2\,x_2 + x_2^2\right]}$$

or,

$$\ln(f_2) = \left(A_1^G/RT\right)\,[1-x_2]^2$$

In fact the equation reported by Jost et al. [4] has this form.

Rather than using the Redlich-Kister equation, recently attention has been directed to the Wilson equation [5] written in equation (l) for a two-component liquid [6].

$$G_m^E/RT = -x_1\,\ln(x_1+\Lambda_{12}\,x_2) - x_2\,\ln(x_2+\Lambda_{21}\,x_1)$$

Then , for example [7],

$$\ln(f_1) = -\ln(x_1+\Lambda_{12}\,x_2) + x_2\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}\,x_2} - \frac{\Lambda_{21}}{\Lambda_{21}\,x_1+x_2}\right)$$

The Wilson equation forms the basis for two further developments, described as the NRTL (non-random, two-liquid) equation [8-10] and the UNIQUAC equation [9-10]. Nevertheless Douheret et al. [11] show how an excess property must be carefully defined. Davis et al. have explored how excess molar properties for liquid mixtures can be analysed in terms of different mole fraction domains [12].

Footnotes

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$$\frac{1}{RT}\,\frac{dG_m^E}{dx_1} = -\ln(x_1+\Lambda_{12}\,x_2) - \frac{x_1\,(1-\Lambda_{12})}{x_1+\Lambda_{12}\,x_2} + \ln(\Lambda_{21}\,x_1+x_2) - \frac{x_2\,(\Lambda_{21}-1)}{\Lambda_{21}\,x_1+x_2}$$

Then using equation (f) with $1-x_1=x_2$,

$$\ln(f_1) = -x_1\,\ln(x_1+\Lambda_{12}\,x_2) - x_2\,\ln(\Lambda_{21}\,x_1+x_2) - x_2\,\ln(x_1+\Lambda_{12}\,x_2) - \frac{x_1\,x_2\,(1-\Lambda_{12})}{x_1+\Lambda_{12}\,x_2} + x_2\,\ln(\Lambda_{21}\,x_1+x_2) + \frac{(x_2)^2\,(1-\Lambda_{21})}{\Lambda_{21}\,x_1+x_2}$$

Or,

$$\ln(f_1) = -(x_1+x_2)\,\ln(x_1+\Lambda_{12}\,x_2) + x_2\left[\frac{\Lambda_{12}\,x_1-x_1}{x_1+\Lambda_{12}\,x_2} - \frac{\Lambda_{21}\,x_2-x_2}{\Lambda_{21}\,x_1+x_2}\right]$$

But

$$\Lambda_{12}\,x_1 - x_1 = \Lambda_{12}\,(1-x_2) - x_1 = \Lambda_{12} - (x_1+\Lambda_{12}\,x_2)$$

Hence,

$$\ln(f_1) = -\ln(x_1 + \Lambda_{12}\, x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}\, x_2} - \frac{\Lambda_{21}}{\Lambda_{21}\, x_1 + x_2}\right]$$

Or,

$$\ln(f_1) = -\ln(x_1 + \Lambda_{12}\, x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}\, x_2} - \frac{\Lambda_{21}}{\Lambda_{21}\, x_1 + x_2}\right]$$

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$$X_m^E = x_1\ (1 - x_1) \sum_{i=1}^{i=k} B_i\ (1 - 2\,x_1)^{i-1}$$

Then $A_i = B_i\,(-1)^i$

J. D. G. de Oliveira and J. C. R.Reis, Thermochim. Acta 2008,468, 119

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1.10.31: Gibbs Energies- Liquid Mixtures- Ideal

The molar Gibbs energy of mixing for an ideal binary liquid mixture is given by equation (a);

$$\Delta_{\text{mix}}\ \mathrm{G_m(id)} = \mathrm{R\,T}\ [\mathrm{x_1}\ \ln \mathrm{x_1} + \mathrm{x_2}\ \ln \mathrm{x_2}]$$

$$\Delta_{\text{mix}}\ \mathrm{G_m(id)/R\,T} = \mathrm{x_1}\ \ln \mathrm{x_1} + \mathrm{x_2}\ \ln \mathrm{x_2}$$

In fact the molar Gibbs energy of mixing for an ideal binary mixture is negative across the complete composition range. According to Gibbs - Helmholtz equation, the molar enthalpy of mixing for an ideal binary mixture is given by equation (c).

$$\Delta_{\text{mix}}\mathrm{H_m(id)} = \frac{\mathrm{d}}{\mathrm{d}\,(\mathrm{T^{-1}})}\left[\frac{\Delta_{\text{mix}}\mathrm{G(id)}}{\mathrm{T}}\right]_{\mathrm{p}}$$

But mole fractions are not dependent on temperature. Hence,

$$\Delta_{\text{mix}}\ \mathrm{H_m(id)} = 0$$

This important result offers a point of reference. At fixed pressure, the mixing of two liquids to form an ideal binary liquid mixture is athermal. Hence a recorded heat of mixing is a direct measure of the extent to which the properties of a given mixture differ from those defined as ideal. But,

$$\Delta_{\text{mix}}\ \mathrm{G_m(id)} = \Delta_{\text{mix}}\mathrm{H_m(id)} - \mathrm{T}\,\Delta_{\text{mix}}\ \mathrm{S_m(id)}$$

For an ideal binary liquid mixture the partial molar entropies of the two liquid components are given by the following equations.

$$\mathrm{S_1(mix;id)} = \mathrm{S_1^*}(\ell) - \mathrm{R}\ \ln(\mathrm{x_1})$$

$$S_2(\mathrm{mix;id}) = \mathrm{S_2^*}(\ell) - \mathrm{R}\ \ln(\mathrm{x_2})$$

$$\mathrm{S_m(mix;id)} = \mathrm{x_1}\ [\mathrm{S_1^*}(\ell) - \mathrm{R}\ \ln(\mathrm{x_1})] + \mathrm{x_2}\ [\mathrm{S_2^*}(\ell) - \mathrm{R}\ \ln(\mathrm{x_2})]$$

From equation (h),

$$\Delta_{\text{mix}}\mathrm{S_m(id)} = -\mathrm{R}\ [\mathrm{x_1}\ \ln \mathrm{x_1} + \mathrm{x_1}\ \ln \mathrm{x_2}]$$

or,

$$\mathrm{T}\,\Delta_{\text{mix}}\ S_m(\ \mathrm{id}\ ) = -RT\,[x_1\ \ln x_1 + x_2\ \ln x_2]$$

But across the complete mole fraction range $[x_1\ \ln x_1 + x_2\ \ln x_2] \leq 0$. Over the same range,

$$\mathrm{T}\,\Delta_{\text{mix}}\mathrm{S_m(id)} > 0$$

Thus the sign and magnitude of $\Delta_{\text{mix}}\mathrm{G_m(id)}$ and (with opposite sign) $\mathrm{T}\,\Delta_{\text{mix}}\mathrm{S_m(id)}$ are defined. A further consequence of equation (d) is that the corresponding isobaric heat capacity variable, $\Delta_{\text{mix}}\mathrm{C_{pm}(id)}$ is zero across the whole mole fraction range. Using equation (a), the molar volume of mixing is given by equation (l). Thus,

$$\Delta_{\text{mix}}\ V_m(\mathrm{id}) = \frac{\partial}{\partial p}[\Delta_{\text{mix}}\ G_m(\mathrm{id})]_p$$

Hence for a binary liquid mixture having ideal properties, across the complete mole fraction range, $\Delta_{\text{mix}}\mathrm{V_m(id)} = 0$. The latter condition requires that the volume of a liquid mixture equals the sum of the volumes of the two liquid components used to prepare the mixture at fixed temperature and pressure. For such a mixture,

$$\mathrm{V_{mix}}\ (\mathrm{id}) = \mathrm{V_2^*}(\ell) + \mathrm{x_1}\ [\mathrm{V_1^*}(\ell) - \mathrm{V_2^*}(\ell)]$$

This simple pattern is not observed. In fact the molar volume of a real binary mixture is usually less than \(\mathrm{V}_{\text{mix}}\ (\text{id})\).

With the benefit of hindsight, we distinguish between Gibbsian and non-Gibbsian on the one hand and between first and second law (thermodynamic) variables on the other hand. Variables H, V and $\mathrm{C_p}$ are Gibbsian first law variables such that the molar property of an ideal binary liquid mixture is given by the mole fraction weighted sum of the properties of the pure liquids. However

Gibbsian second law properties (e.g. entropies and Gibbs energies) require combinatorial terms arising from the irreversible entropy of mixing.

These simple rules do not apply in the case of molar non-Gibbsian properties (e.g. isentropic compressions and isochoric heat capacities) of ideal mixtures.

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1.10.32: Gibbs Energies- Liquid Mixtures- Typically Aqueous (TA)

For many binary aqueous liquid mixtures, the pattern shown by the molar excess thermodynamic parameters is $G_m^E > 0$; $|T S_m^E| > |H_m^E|$. This pattern of excess molar properties defines TA mixtures. ${G_m}^E$ is positive because the excess molar entropy of mixing is large in magnitude and negative in sign. In these terms mixing is dominated by the entropy change. The excess molar enthalpy of mixing is smaller in magnitude than either ${G_m}^E$ or $T\,{G_m}^E$ but exothermic in water-rich mixtures.

The word 'Typically' in the description stems from observation that this pattern in thermodynamic variables is rarely shown by non-aqueous systems. At the time the classification was proposed [1], most binary aqueous liquid mixtures seemed to follow this pattern. Among the many examples of this class of system are aqueous mixtures formed by ethanol, 2-methyl propan-2-ol and cyclic ethers including tetrahydrofuran[2]. In water-rich mixtures, a large in magnitude but negative in sign $T\,{S_m}^E$ produces a large (positive) ${G_m}^E$. For mixtures rich in the apolar component m endothermic mixing produces a positive ${G_m}^E$. The key point is that in m water-rich mixtures a positive ${G_m}^E$ emerges from a negative $T\,{S_m}^E$.

With reference to volumetric properties of these system, the partial molar volume $V(ROH)$ for monohydric alcohols can be extrapolated to infinite dilution; i.e. $\lim (x_2 \to 0)\, V(ROH) = V(ROH; aq)^\infty$ where x_2 is the mole fraction of alcohol. The difference, $[V(ROH; aq)^\infty - V^*(ROH; \ell)]$ is negative. In fact this pattern is observed for both TA and Typical Non-aqueous binary aqueous mixtures. Examples where this pattern is observed included aqueous mixtures formed by DMSO, H_2O_2 and CH_3CN. Significantly $[V(ROH; aq) - V^*(ROH; \ell)]$ is negative for TA mixtures, decreasing from $[V(ROH; aq)^\infty - V^*(ROH; \ell)]$ with increase in mole fraction of ROH, accompanying by a tendency to immiscibility. The initial decrease in $[V(ROH; aq) - V^*(ROH; \ell)]$ with increase in x_2 is more dramatic the more hydrophobic the non-aqueous component; for 2-methyl propan-2-ol aqueous mixtures at $298.2\ K$ and ambient pressure, the minimum occurs at an alcohol mole fraction 0.04 (at $298.2\ K$).

Many explanations have been offered for the complicated patters shown by the dependence of $[V(ROH; aq) - V^*(ROH; \ell)]$ on mole fraction composition.

In one model, the negative $[V(ROH; aq) - V^*(ROH; \ell)]$ at low mole fractions of ROH is accounted for in terms of a liquid clathrate in which part of the hydrophobic R-group 'occupies' a guest site in the water lattice. The decrease in $[V(ROH; aq) - V^*(ROH; \ell)]$ is accounted for in terms of an increasing tendency towards a clathrate structure. But with increase in x_2 there comes a point where there is insufficient water to construct a liquid clathrate water host. Hence $[V(ROH; aq) - V^*(ROH; \ell)]$ increases.

An important characteristic of TA mixtures is a tendency towards and in some cases actual decrease in liquid miscibility with increase in temperature. At ambient T and p, the mixture 2-methyl propan-2-ol + water is miscible (but only just!) in all molar proportions. The corresponding mixtures prepared using butan-1-ol and butan-2-ol are partially miscible. TA systems are therefore often characterised by a Lower Critical Solution Temperature LCST. In fact nearly all examples quoted in the literature of systems having an LCST involve water as one component; e.g. $LCST = 322\ K$ for 2-butoxyethanol + water [3]. This tendency to partial miscibility is often signalled by the properties of the completely miscible systems.

Returning to the patterns shown by relative partial molar volumes, $[V(ROH; aq) - V^*(ROH; \ell)]$, a stage is reached whereby with increase in mole fraction of the non-aqueous component, this property increases after a minimum. Other properties of the mixtures also change dramatically including a marked increase in (α_a/v^2) where α_a is the amplitude attenuation constant and ν is the frequency of the sound wave in the MHz range; e.g. $70\ MHz$. Actually the pattern is complicated. Over the range of mixture mole fractions x_2 where $[V(ROH; aq) - V^*(ROH; \ell)]$ decreases with increase in x_2, the ratio (α_a/v^2) hardly changes although the speed of sound increases. At a mole fraction x_2 characteristic of the temperature and the non-aqueous component, (α_a/v^2) increases sharply, reaching a maximum where the mixture has a strong tendency to immiscibility. This interplay between in-phase and out-of-phase components of the complex isentropic compressibility when the mole fraction composition of the mixture is changed highlights the molecular complexity of these systems. By way of contrast the ratio (α_a/v^2) for DMSO + water mixtures (a TNAN system) changes gradually when the mole fraction of DMSO is changed.

For TA mixtures where (α_a/v^2) is a maximum [4], other evidence points to the fact these mixtures are micro-heterogeneous; cf. excess molar isobaric heat capacities. Phase separation of the mixture 2-methyl propan-2-ol is observed when butane gas is dissolved in the liquid mixture. The miscibility curve shows an LCST near $282\ K$ [5].

Footnotes

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1.10.33: Gibbs Energies- Liquid Mixtures- Typically Non-Aqueous Positive; TNAP

For this sub-group of binary aqueous liquid mixtures, $G_m{}^E$ is positive. An example of such a mixture is ‘water + ethanenitrile’. The positive $G_m{}^E$ reflects endothermic mixing across nearly all the mole fraction range. These mixtures have a tendency to be partially miscible with an Upper Critical Solution Temperature, UCST. For aqueous mixtures the composition at the UCST is often ‘water-rich’. For ethanenitrile + water, the UCST is $272\ \mathrm{K}$. The positive $G_m{}^E$ and endothermic mixing are attributed to disruption of water-water hydrogen bonding by added mathrm{MeCN}; cf. $CCl_4 + \ MeOH$ [1,2].

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1.10.34: Gibbs Energies- Liquid Mixtures- Typically Non-Aqueous Negative; TNAN

For this sub-group, G_m^E is negative because there is strong inter- m component interaction which also produces exothermic mixing [1-4]. Examples of aqueous mixtures which fall into this class are

i. water + DMSO and
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1.10.35: Gibbs Energies- Liquid Mixtures- Immiscibility

For a given binary liquid mixture (at defined T and p) characterised by a plot of excess Gibbs energy ${\mathrm{G_m}}^{\mathrm{E}}$ against mole fraction, ${\mathrm{G_m}}^{\mathrm{E}}$ can be positive. Indeed if $[\mathrm{G_m^E}/\mathrm{R\,T}]$ strongly exceeds 0.5, the mixture is partially miscible. That is to say the liquid comprises two liquid phases having different mole fraction compositions.

A fascinating variety of patterns emerge in the context of partial miscibilities.

a. Some binary liquid mixtures are completely miscible but become partially miscible with increase in temperature. The corresponding miscibility curve has a minimum at a Lower Critical Solution Temperature, LCST. For example in the case of 2-butoxyethanol + water , the LCST is at $322.2\ \mathrm{K}$ where $x\,(\mathrm{H_2O}) = 0.942$ [1]. In fact all commonly quoted examples of this class of systems have water as one component. A fascinating example concerns propionitrile+ polystyrene mixtures. The miscibility curves indicate that the LCST occurs at negative pressures; in effect when the mixture is ‘stretched’ [2].
b. Many binary liquid mixtures (e.g/ phenol + water has (at ambient pressure).are partially miscible, becoming completely miscible on raising the temperature. The miscibility curve has a maximum at an Upper Critical Solution Temperature, UCST. At ambient pressure a small number of liquid mixtures exhibit both UCST and LCST. In other words the miscibility plot forms a closed loop.

Partial miscibility plots also show deuterium isotope effects. In the case of $\mathrm{CH_3CN} + \mathrm{H_2O}\,(\mathrm{component\ 2} = \mathrm{CH_3CN})$ the UCST is $272.10\ \mathrm{K}$ at $x_2 = 0.38$ [2].

Footnotes

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1.10.36: Gibbs Energies- Salt Solutions- Aqueous Mixtures

The solubilities of chemical substance j in two liquids ℓ_1 and ℓ_2 (at the same T and p) offers a method for comparing the reference chemical potentials, using the transfer parameter $\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu_{\mathrm{j}}^0$. A similar argument is advanced in the context of salt solutions in which comparison of the solubility of salt j in two liquids leads to the transfer parameter for the salt. However the argument does not stop there. In the case of, for example a 1:1 salt $\mathrm{M}^{+}\mathrm{X}^{-}$, the derived transfer for the salt is re-expressed as the sum of transfer parameters for the separate ions M^{+} and X^{-}. Thus

$$\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu^0\left(\mathrm{M}^{+}\mathrm{X}^{-}\right)=\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu^0\left(\mathrm{M}^{+}\right)+\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu^0\left(\mathrm{X}^{-}\right)$$

However granted that we can obtain an estimate of the transfer parameter for the salt, $\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu^0\left(\mathrm{M}^{+}\mathrm{X}^{-}\right)$, thermodynamics does not offer a method for calculating the corresponding ionic transfer parameters. Several extra-thermodynamic procedures yield estimated single ion thermodynamic transfer parameters. The simplest approach adopts a reference ion (e.g. H^{+}) and reports relative transfer ionic chemical potentials.

$$\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu^0\left(\mathrm{H}^{+}\right)=0$$

For example;

$$\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu^0\left(\mathrm{C}\ell^{-}\right)=\Delta\left(\ell_1 \rightarrow \ell_2\right) \mu^0(\mathrm{HC}\ell)$$

Solubilities and Transfer Parameters

A closed system (at fixed T and ambient pressure) contains a solid salt j in equilibrium with salt j in aqueous solution. At equilibrium,

$$\mu_{\mathrm{j}}^*(\mathrm{~s})=\mu_{\mathrm{j}}^0(\mathrm{aq})+\mathrm{v} \mathrm{R} \mathrm{T} \ln \left(\mathrm{Q} \mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq}) \gamma_{\pm}^{\mathrm{eq}}(\mathrm{aq}) / \mathrm{m}^0\right)$$

Similarly for an equilibrium system where the solvent is a binary aqueous mixture, mole fraction x_2,

$$\mu_{\mathrm{j}}^*(\mathrm{~s})=\mu_{\mathrm{j}}^0(\mathrm{~s} \ln ; \mathrm{x}_2)+\mathrm{v} \mathrm{R} \mathrm{T} \ln \left(\mathrm{Q} \mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}\left(\mathrm{s} \ln ; \mathrm{x}_2\right) \gamma_{\pm}^{\mathrm{eq}}\left(\mathrm{s} \ln ; \mathrm{x}_2\right) / \mathrm{m}^0\right)$$

Then,

$$\begin{aligned}\Delta\left(\mathrm{aq} \rightarrow \mathrm{x}_2\right) \mu_{\mathrm{j}}^0(\mathrm{~s} \ln) & =\mu_{\mathrm{j}}^0(\mathrm{~s} \ln ; \mathrm{x}_2)-\mu_{\mathrm{j}}^0(\mathrm{aq}) \\ & =-\mathrm{v} \mathrm{R} \mathrm{T} \ln \left[\mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}\left(\mathrm{s} \ln ; \mathrm{x}_2\right) \gamma_{\pm}^{\mathrm{eq}}\left(\mathrm{s} \ln ; \mathrm{x}_2\right) / \mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq}) \gamma_{\pm}^{\mathrm{eq}}(\mathrm{aq})\right]\end{aligned}$$

A key assumption sets the ratio of mean ionic activity coefficients to unity. In effect we assume that the solubilities do not change dramatically as x_2 is changed. Therefore,

$$\Delta\left(\mathrm{aq} \rightarrow \mathrm{x}_2\right) \mu_{\mathrm{j}}^0(\mathrm{~s} \ln)=-\mathrm{v} \mathrm{R} \mathrm{T} \ln \left[\mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}\left(\mathrm{s} \ln ; \mathrm{x}_2\right) / \mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq})\right]$$

Thus the ratio $\left[\mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}\left(\mathrm{s} \ln ; \mathrm{x}_2\right) / \mathrm{m}_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq})\right]$ is effectively the ratio of solubilities of salt j in the mixed aqueous solutions and aqueous solution. If the solubility of the salt increases with increase in x_2, $\Delta\left(\mathrm{aq} \rightarrow \mathrm{x}_2\right) \mu_{\mathrm{j}}^0(\mathrm{~s} \ln)$ is negative. In other words, the salt in aqueous solutions is stabilised by adding the co-solvent.

Granted that solubility data lead to an estimate for $\Delta\left(\mathrm{aq} \rightarrow \mathrm{x}_2\right) \mu_{\mathrm{j}}^0(\mathrm{~s} \ln)$, this quantity involves contributions from both cations and anions. For a salt containing two ionic substances

$$\Delta\left(\mathrm{aq} \rightarrow \mathrm{x}_2\right) \mu_{\mathrm{j}}^0(\mathrm{~s} \ln)=\Delta\left(\mathrm{aq} \rightarrow \mathrm{x}_2\right) \mu_{+}^0(\mathrm{~s} \ln)+\Delta\left(\mathrm{aq} \rightarrow \mathrm{x}_2\right) \mu_{-}^0(\mathrm{~s} \ln)$$

The background to this type of analysis centres on classic studes into the electrical conductivities of salt solutions. For a given salt in a solvent (at fixed T and p), the molar conductivity approaches a limiting value with decrease in concentration; $\operatorname{limit}\left(c_j \rightarrow 0\right) \Lambda_j = \Lambda_j^0$. The limiting molar conductivity of a salt solution ${\Lambda^0}_j$ containing a 1:1 salt can be written as the sum of limiting ionic conductivities ${\lambda_i}^0$ of anions and cations.

$$\Lambda_{\mathrm{j}}^0=\lambda_{+}^0+\lambda_{-}^0$$

The transport number of an ion t_j measures the ratio λ_j^0/Λ. Both t_j and Λ can be measured and hence λ_j^0 calculated in the limit of infinite dilution characterizes ion j in a given solvent at defined T and p. Discrimination between anions and cations arises from their electrical charges and hence the direction of migration of ions in an electric field. Nevertheless the task of measuring both t_j and Λ is not trivial and some simple working hypothesis is often sought. The argument is advanced that the molar conductivities are equal in magnitude for two ions having similar size and solvation characteristics. This 'extrathermodynamic' assumption has been applied [1-8] to a range of 'onium salts including

1. Bu_4N^+ Ph_3FB^-,
2. iso $-Bu_3N^+$ H Ph_4B^-,
3. Bu_4N^+ Ph_4B^-,
4. iso $-Am_3BuN^+$ H_4B^-
5. iso $-Am_4N^+$ iso $-Am_4$ B^-; so λ^0 (big cation) = λ^0 (big anion).

This 'big ion – big ion' assumption is carried over to the analysis of thermodynamic properties where we lack the discrimination between cations and anions based on their mobilities in an applied electric potentials. gradient. Then for example the change in solubility of one such salt in aqueous solution on adding a cosolvent (e.g. ethanol) can be understood in terms of equal transfer thermodynamic potentials.

$$(1/2)\,\Delta\,(\mathrm{aq} \rightarrow \mathrm{x_2})\,\mu^0(\text{ big cation big anion; s ln}) = \Delta\,(\mathrm{aq} \rightarrow \mathrm{x_2})\,\mu^0(\text{ big cation; s ln})$$
$$= \Delta\,(\mathrm{aq} \rightarrow \mathrm{x_2})\,\mu^0(\text{ big anion; l ln})$$

For example having obtained $\Delta\,(\mathrm{aq} \rightarrow \mathrm{x_2})\,\mu^0(\text{ big cation; ln})$, the difference in solubilities of the corresponding salt iodide is used to obtain the transfer parameter for iodide ions in the two solvents.

$$\Delta(\mathrm{aq} \rightarrow \mathrm{x_2})\,\mu^0\,(\mathrm{I^-}; \mathrm{s\,ln}) =$$
$$\Delta\,(\mathrm{aq} \rightarrow \mathrm{x_2})\,\mu^0(\text{ big cation iodide; s ln}) - \Delta\,(\mathrm{aq} \rightarrow \mathrm{x_2})\,\mu^0(\text{ big cation s ln})$$

Considerable information is available in the chemical literature concerning ionic transfer parameters, particularly for solutes in binary aqueous mixtures at 298.2 K and ambient pressure.[8-21] Unfortunately there is no agreed composition scale for transfer parameters. Information includes transfer parameters based on concentration, molality and mole fractions scales for the solutes. The situation is further complicated by the fact that different scales are used to express composition of liquid mixtures. Common scales include mass%, mole fraction and vol%. Conversion between these scales is a tedious. Some examples of the required equations are presented in an Appendix to this Topic.

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Appendix

Conversion between Composition Scales: Aqueous Solutions.

Molality and Mole Fraction

Solute j in Aqueous Solution

We write down two equations for the same quantity, the chemical potential of solute j. For the chemical potential of solute j in an ideal aqueous solution at ambient pressure (i.e. close to the standard pressure, p^0),

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0\left(\mathrm{aq};\mathrm{m}^0\right) + \mathrm{R\,T\,ln}\left[\mathrm{m_j}/\mathrm{m}^0\right]$$

Here m_j is the molality of solute j; $\mathrm{m}^0 = 1\ \mathrm{molkg}^{-1}$, the reference molality. However we may decide to express the composition of the solution in terms of the mole fraction of solute. If the properties of the solute are ideal, the chemical potential of solute j, $\mu_j(\mathrm{aq})$ is related to the mole fraction of solute x_j.

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0\left(\mathrm{aq};\mathrm{x_j}=1\right) + \mathrm{R\,T\ ln}\left[\mathrm{x_j}\right]$$

Equations (i) and (ii) describe the same property, $\mu_j(\mathrm{aq})$. The property $\mu_j^0\left(\mathrm{aq};x_j=1\right)$ is interesting because it describes the chemical potential of solute j in aqueous solution where the mole fraction of solute is unity; it is clearly an 'extrapolated' property of the solute.

If n_j is the amount of solute in a solution prepared using $10^2\ \mathrm{kg}$ of water, we can combine equations (i) and (ii); $\mathrm{x_j} = \mathrm{n_j}/\left[\left(10^2/\mathrm{M}_1\right) + \mathrm{n_j}\right]$ where for a dilute solution $\left(10^2/\mathrm{M}_1\right) >> \mathrm{n_j}$; M_1 is the molar mass of water.

$$\mu_\mathrm{j}^0\left(\mathrm{aq};\mathrm{m}^0\right) + \mathrm{R\,T\ ln}\left[\mathrm{n_j}/10^2\,\mathrm{m}^0\right] = \mu_\mathrm{j}^0\left(\mathrm{aq};\mathrm{x_j}=1\right) + \mathrm{R\,T\ ln}\left[\mathrm{n_j\,M_1}/10^2\right]$$

Or,

$$\mu_\mathrm{j}^0\left(\mathrm{aq};\mathrm{m}^0\right) - \mu_\mathrm{j}^0\left(\mathrm{aq};\mathrm{x_j}=1\right) = \mathrm{R\,T\ ln}\left[\mathrm{m}^0\,\mathrm{M}_1\right]$$

We note that $\left[\mathrm{m}^0\,\mathrm{M}_1\right] = \left[\mathrm{molkg}^{-1}\right]\ \left[\mathrm{kgmol}^{-1}\right] = [1]$

Solute j in a Solvent prepared as a Binary Aqueous Mixture

If n_j is the amount of solute j in $10^2\ \mathrm{kg}$ of a solvent mixture, the chemical potential of solute j is given by equation (iv)

$$\mu_\mathrm{j}(\mathrm{mix}) = \mu_\mathrm{j}^0\left(\mathrm{mix};\mathrm{m}^0\right) + \mathrm{R\,T\ ln}\left[\mathrm{n_j}/10^2\,\mathrm{m}^0\right]$$

We note that $\left[\mathrm{n_j}/10^2\,\mathrm{m}^0\right] = \left[\mathrm{mol/kg\,mol\,kg}^{-1}\right] = [1]$. If the binary solvent mixture comprises $w_2\%$ of the non-aqueous component, for a dilute solution of solute j, the mole fraction of solute x_j is given by equation (vi) where M_2 is the molar mass of the cosolvent.

$$\mathrm{x_j} = \frac{\mathrm{n_j}}{\left\{\left[\left(10^2 - \mathrm{w_2\%}\right]/\mathrm{M}_1\right\} + \left\{\mathrm{w_2\%}/\mathrm{M}_2\right\}}$$

Using the mole fraction scale for solute j, the chemical potential of solute j in the mixture, composition $w_2\%$ is given by equation (vii).

$$\mu_\mathrm{j}(\mathrm{mix}) = \mu_\mathrm{j}^0\left(\mathrm{mix};\mathrm{x_j}=1\right) + \mathrm{R\,T\ ln}\left[\frac{\mathrm{n_j}}{\left\{\left[\left(10^2 - \mathrm{w_2\%}\right]/\mathrm{M}_1\right\} + \left\{\mathrm{w_2\%}/\mathrm{M}_2\right\}}\right]$$

Equations (v) and (vii) describe the same property, the chemical potential of solute j in a mixed solvent system. Hence,

$$\mu_\mathrm{j}^0\left(\mathrm{mix};\mathrm{m}^0\right) + \mathrm{R\,T\ ln}\left[\mathrm{n_j}/10^2\,\mathrm{m}^0\right] = \mu_\mathrm{j}^0\left(\mathrm{mix};\mathrm{x_j}=1\right) + \mathrm{R\,T\ ln}\left[\frac{\mathrm{n_j}}{\left\{\left[\left(10^2 - \mathrm{w_2\%}\right]/\mathrm{M}_1\right\} + \left\{\mathrm{w_2\%}/\mathrm{M}_2\right\}}\right]$$

Or,

$$\mu_j^0\left(\text{mix};\text{m}^0\right) = \mu_j^0\left(\text{mix};\text{x}_j=1\right) + \text{R T ln}\left[\frac{10^2\,\text{m}^0}{\left\{\left[\left(10^2-\text{w}_2\%\right]/\text{M}_1\right\}+\left\{\text{w}_2\%/\text{M}_2\right\}}\right]$$

Conversion of Scales.

It is convenient at this point to comment on the difference in reference chemical potentials of solute j in aqueous solutions and a solvent mixture. Thus from equation (iv).

$$\mu_j^0\left(\text{aq};\text{m}^0\right) - \mu_j^0\left(\text{aq};\text{x}_j=\text{l}\right) = \text{R T ln}\left[\text{m}^0\,\text{M}_1\right]$$

And from equation (ix)

$$\mu_j^0\left(\text{mix};\text{m}^0\right) - \mu_j^0\left(\text{mix};\text{x}_j=1\right) = \text{R T ln}\left[\frac{10^2\,\text{m}^0}{\left\{\left[\left(10^2-\text{w}_2\%\right]/\text{M}_1\right\}+\left\{\text{w}_2\%/\text{M}_2\right\}}\right]$$

The difference between equations (x) and (xi) yields an equation relating transfer parameters for solute j on the two composition scales.

$$\mu_j^0\left(\text{mix};\text{m}^0\right) - \mu_j^0\left(\text{aq};\text{m}^0\right) = \mu_j^0\left(\text{mix};\text{x}_j=1\right) - \mu_j^0\left(\text{aq};\text{x}_1=1\right) - \text{R T ln}\left[\frac{\left\{10^2-\text{w}_2\%\right\}+\left\{\text{w}_2\%\,\text{M}_1/\text{M}_2\right\}}{10^2}\right]$$

Hence

$$\Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{ m}-\text{scale}) = \Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{x}-\text{ scale }) - \text{R T ln}\left[\frac{\left\{10^2-\text{w}_2\%\right\}+\left\{\text{w}_2\%\,\text{M}_1/\text{M}_2\right\}}{10^2}\right]$$

Or,

$$\Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{ m}-\text{scale}) = \Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{x}-\text{ scale }) - \text{R T ln}\left[1-\left(\text{w}_2\%/10^2\right)+\left(\text{w}_2\%/10^2\right)\,\text{M}_\text{l}/\text{M}_2\right]$$

Or,

$$\Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{ m}-\text{ scale }) = \Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{x}-\text{ scale }) - \text{R T ln}\left\{1-\left[1-\left(\text{M}_1/\text{M}_2\right)\right]\,\left(\text{w}_2\%/10^2\right)\right\}$$

If solute j is a salt which is completely dissociated into ν ions in both aqueous solution and in the mixed solvent system,

$$\Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{ m}-\text{scale}) = \Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{x}-\text{scale}) - \text{v R T ln}\left\{1-\left[1-\left(\text{M}_1/\text{M}_2\right)\right]\,\left(\text{w}_2\%/10^2\right)\right\}$$

Thus for each ionic substance contributing to the transfer property for the salt,

$$\Delta(\text{aq}\rightarrow\text{mix})\mu_j^0(\text{ s ln}) = v_+\,\Delta(\text{aq}\rightarrow\text{mix})\mu_+^0(\text{ s ln}) + v_-\,\Delta(\text{aq}\rightarrow\text{mix})\mu_-^0(\text{ s ln})$$

Equations (xv) and (xvi) show that the difference between the transfer chemical potentials on the x- and m- scales is independent of temperature. The difference is based on the mass of the solvent components in the mixture. Consequently the transfer enthalpies on the two scales are equal.

$$\Delta(\text{aq}\rightarrow\text{mix})\text{H}_j^0(\text{ m}-\text{ scale }) = \Delta(\text{aq}\rightarrow\text{mix})\text{H}_j^0(\text{x}-\text{ scale })$$

Therefore the difference in the transfer chemical potentials can be traced to differences in the transfer entropies. At constant pressure,

$$
\begin{aligned}
&-\Delta(\mathrm{aq} \rightarrow \text{ mix })\mathrm{S}_{\mathrm{j}}^{0}(\text{ m}-\text{ scale }) = \mathrm{d}\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{\mathrm{j}}^{0}/\mathrm{dT} \\
&= -\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mathrm{S}_{\mathrm{j}}^{0}(\mathrm{x}-\text{ scale }) \\
&+ \mathrm{v}\,\mathrm{R}\,\ln\left\{\left[1-\left[1-(\mathrm{M}_1/\mathrm{M}_2)\right]\left(\mathrm{w}_2\%/10^2\right)\right\}\right\}
\end{aligned}
$$

A similar argument notes that the masses of the solvents forming the mixed solvents are independent of pressure (at fixed temperature) Therefore the volumes of transfer on molality and mole fraction scales are equal. In summary (at fixed T and \mathrm{p}\)),

$$
\begin{aligned}
\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{s\,ln}) &= \mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{mix}) - \mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{aq}) \\
&= -\mathrm{T}^2\left[\partial\left\{\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{\mathrm{j}}^{0}(\mathrm{sln};\mathrm{T})/\mathrm{T}\right\}/\mathrm{dT}\right]
\end{aligned}
$$

Further, for the isobaric partial molar heat capacities,

$$
\begin{aligned}
\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mathrm{C}_{\mathrm{pj}}^{\infty}(\mathrm{s\,ln}) &= \mathrm{C}_{\mathrm{pj}}^{\infty}(\mathrm{mix}) - \mathrm{C}_{\mathrm{pj}}^{\infty}(\mathrm{aq}) \\
&= \left[\partial\left\{\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{s\,ln};\mathrm{T})\right\}/\partial\mathrm{T}\right]_{\mathrm{p}}
\end{aligned}
$$

Also

$$
\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{s\,ln}) = \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{mix}) - \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq})
$$

Transfer Parameters: Molality and Concentration Scales.

The procedures described above are repeated but now in a comparison of the molality and concentration scales.

For a solute j (at fixed T and p) in a solution having ideal thermodynamic properties, the chemical potential of solute j is related to concentration of solute j, c_j which by convention is expressed in terms of amount of solute in $1\ \mathrm{dm}^3$ of solution at defined T and p; i.e. $\mathrm{c_j} = [\mathrm{mol\ dm}^{-3}]$. A reference concentration c_r describes a solution where one dm^3 of solution contains one mole of solute. Because the volume of a liquid depends on both temperature and pressure, these variables must be specified. Thus

$$
\mu_j(aq) = \mu_j^0(c-scale;aq) + RT\,\ln\left[c_j(aq)/c_r\right]
$$

The units of both $\mathrm{c}_j(\mathrm{aq})$ and c_r are $[\mathrm{moldm}^{-3}]$.Hence using equations (i) and (xxiii),

$$
\begin{aligned}
\mu_{\mathrm{j}}(\mathrm{aq}) &= \mu_{\mathrm{j}}^{0}(\text{ m};\mathrm{aq}) + \mathrm{R\,T\,ln}\left[\mathrm{m_j(aq)/m}^0\right] \\
&= \mu_{\mathrm{j}}^{0}(\mathrm{c}-\mathrm{scale};\mathrm{aq}) + \mathrm{R\,T\,ln}\left[\mathrm{c_j(aq)/c_r}\right]
\end{aligned}
$$

For a solution in $10^2\ \mathrm{kg}$ of solvent,

$$
\mathrm{m_j(aq)} = \mathrm{n_j}/10^2\ \mathrm{mol\ kg}^{-1}
$$

For a dilute solution, density

$$
\rho(\mathrm{aq}) = \rho_1^*(\ell)
$$

Volume of a dilute solution with mass

$$
10^2\ \mathrm{kg} = 10^2/\rho_1^*(\ell)
$$

Concentration,

$$
\mathrm{c_j} = \mathrm{n_j}\,\rho_{\mathrm{l}}^*(\ell)/10^2
$$

Therefore equation (xxiv) can be written in the following form.

$$
\begin{aligned}
&\mu_{\mathrm{j}}^{0}(\text{ m};\mathrm{aq}) + \mathrm{R\,T\,ln}\left[\mathrm{n_j}/10^2\,\mathrm{m}^0\right] \\
&\qquad = \mu_{\mathrm{j}}^{0}(\mathrm{c}-\mathrm{scale};\mathrm{aq}) + \mathrm{R\,T\,ln}\left[\mathrm{n_j}\,\rho_{\mathrm{l}}^*(\ell)/\mathrm{c_r}\right]
\end{aligned}
$$

For the solution in a binary aqueous mixture,

$$
\begin{aligned}
&\mu_{\mathrm{j}}^{0}(\text{ m};\mathrm{mix}) + \mathrm{R\,T\,ln}\left[\mathrm{n_j}/10^2\,\mathrm{m}^0\right] \\
&\qquad = \mu_{\mathrm{j}}^{0}(\mathrm{c}-\text{ scale};\text{ mix }) + \mathrm{R\,T\,ln}\left[\mathrm{n_j}\,\rho(\mathrm{mix})/\mathrm{c_r}\right]
\end{aligned}
$$

Then,

$$\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{\mathrm{j}}^{0}(\ \mathrm{m}) = \Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{\mathrm{j}}^{0}(\mathrm{c}-\mathrm{scale}) + \mathrm{R\,T}\ \ln\left[\rho(\mathrm{mix})/\rho_{1}^{*}(\ell)\right]$$

In the event that solute is a salt which produces ν moles of ions for each mole of salt,

$$\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{\mathrm{j}}^{0}(\ \mathrm{m}) = \Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{\mathrm{j}}^{0}(\mathrm{c}-\ \mathrm{scale}\ ) + \mathrm{v\,R\,T}\ \ln\left[\rho(\mathrm{mix})/\rho_{1}^{*}(\ell)\right]$$

For each ionic substances, e.g. a cation

$$\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{+}^{0}(\ \mathrm{m}) = \Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mu_{+}^{0}(\mathrm{c}-\mathrm{scale}) + \nu\,\mathrm{R\,T}\ \ln\left[\rho(\mathrm{mix})/\rho_{1}^{*}(\ell)\right]$$

Because the densities of water and each mixture depends on temperature at fixed pressure, the transfer enthalpies on molality and concentration scales differ. Thus

$$\Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mathrm{H}_{+}^{\infty}(\mathrm{m}) = \Delta(\mathrm{aq} \rightarrow \mathrm{mix})\mathrm{H}_{+}^{\infty}(\mathrm{c}-\mathrm{scale}) - \mathrm{v\,R\,T}^{2}\ \left[\partial \ln\left[\rho(\mathrm{mix})/\rho_{1}^{*}(\ell)\right]/\partial \mathrm{T}\right]_{\mathrm{p}}$$

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SECTION OVERVIEW

1.11: Gibbs-Duhem Equation

1.11.1: Gibbs-Duhem Equation

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1.11.1: Gibbs-Duhem Equation

This equation is at the heart of chemical thermodynamics. The Gibbs energy of a closed system can be expressed as follows.

$$\mathrm{G} = \mathrm{G}\left[\mathrm{T}, \mathrm{p}, \mathrm{n_i}\right]$$

Here $\mathrm{n_i}$ represents the amounts of all chemical substances in the system. Then for a system containing two chemical substances, 1 and 2,

$$\mathrm{G} = \mathrm{G}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2\right]$$

If we prepare a system containing $\mathrm{k\ n}_1$ and $\mathrm{k\ n}_2$ moles of the two chemical substances [cf. Euler's Theorem], the Gibbs energy increases by a factor, k. Hence,

$$\mathrm{G} = \mathrm{n}_1\,\mu_1 + \mathrm{n}_2\,\mu_2$$

In general [1],

$$\mathrm{G} = \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{n_j}\,\mu_\mathrm{j}$$

Equation (c) is differentiated [2].

$$\mathrm{dG} = \mathrm{n}_1\,\mathrm{d}\mu_1 + \mu_1\,\mathrm{dnn}_1 + \mathrm{n}_2\,\mathrm{d}\mu_2 + \mu_2\,\mathrm{dn}_2$$

But [3],

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} + \mu_1\,\mathrm{dn}_1 + \mu_2\,\mathrm{dn}_2$$

Therefore, combining equations (c) and (f),

$$-S\,dT + V\,dp - n_1\,d\mu_1 - n_2\,d\mu_2 = 0$$

Therefore, for a system held at fixed T and p [4],

$$\mathrm{n}_1\,\mathrm{d}\mu_1 + \mathrm{n}_2\,\mathrm{d}\mu_2 = 0$$

Equation (h) expresses the 'communication' between the two chemical substances in the system. In some senses equation (h) is a Happy Family Equation. If the chemical potential of substance 1, μ_1 increases [i.e. $\mathrm{d}\mu_1 > 0$], the chemical potential of chemical substance 2 decreases, [i.e. $\mathrm{d}\mu_2 < 0$], in order to hold the condition expressed by equation (h) [5].

Footnotes

[1] Similarly $\mathrm{U} = \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{n_j}\,\mu_\mathrm{j} + \mathrm{T\,S} - \mathrm{p\,V}$ $\mathrm{H} = \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{n_j}\,\mu_\mathrm{j} + \mathrm{T\,S}$ and $F = \sum_{j=1}^{j=i} n_j\,\mu_j - p\,V$

[2] Generally, $\mathrm{dG} = \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \left[\mathrm{n_j}\,\mathrm{d}\mu_\mathrm{j} + \mu_\mathrm{j}\,\mathrm{dnn_j}\right]$

[3] Generally \(\mathrm{dG}=-\mathrm{S} \, \mathrm{dT}+\mathrm{V} \, \mathrm{dp}+\sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mu_{\mathrm{j}} \, \mathrm{dn}_{\mathrm{j}}\)

[4] Generally $\sum_{j=1}^{j=i} n_j\,d\mu_j = 0$

[5] If one member of a family is sad for some reason, other members of the family say something along the lines, 'cheer up --it is not as bad as all that'. If another member of the family becomes over-excited, the family says something along the lines, 'calm down'. Similar things happen to chemical substances in a closed system at fixed T and p.

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1.11.2: Gibbs-Duhem Equation- Salt Solutions- Osmotic and Activity Coefficients

We consider an aqueous solution prepared using $1\ \mathrm{kg}$ of solvent, water, at temperature T and pressure p ($\cong p^0$). For an aqueous salt solution, the chemical potential $\mu_j(\mathrm{aq})$ for salt j at molality m_j is given by equation (a) where $\gamma_\pm$ is the mean ionic activity coefficient of the salt.

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{v\,R\,T\ ln}\left(\mathrm{Q\,m_j\,\gamma_\pm/m^0}\right)$$

By definition, at all T and p,

$$\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\gamma_\pm = 1$$

For the solvent, water,

$$\mu_1(\mathrm{aq}) = \mu_1^\star(\ell) - \mathrm{v\,R\,T}\,\phi\,\mathrm{M_1\,m_j}$$

By definition, at all T and p,

$$\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\phi = 1.0$$

Chemical potentials $\mu_j(\mathrm{aq})$ and $\mu_1(\mathrm{aq})$ are linked by the Gibbs-Duhem equation. This,

$$(1/M_1)\ d\mu_1(aq) + v\,m_j\,d\mu_j(aq) = 0$$

$$\begin{aligned}(1/\mathrm{M_1})\ \mathrm{d}\left[\mu_1^*(\ell) - \mathrm{v\,R\,T}\,\phi\,\mathrm{M_1\,m_j}\right]\\ +\mathrm{v\,m_j\,d}\left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{v\,R\,T\ ln}\left(\mathrm{Q\,m_j\,\gamma_\pm/m^0}\right)\right] = 0\end{aligned}$$

$$\begin{aligned}-v\,R\,T\,d\left[\phi\,m_j\right]\\ +v\,m_j\,v\,R\,T\,d\left[\ln(Q) + \ln\left(m_j\right) + \ln\left(\gamma_\pm\right) - \ln\left(m^0\right)\right] = 0\end{aligned}$$

$$-\mathrm{d}\left[\phi\,\mathrm{m_j}\right] + \mathrm{v\,m_j}\ \left\{\mathrm{d\ln\left(m_j\right) + d\ln\left(\gamma_\pm\right)}\right\} = 0$$

$$-\phi\,dm_j - m_j\,d\phi + v\,m_j\,d\ln\left(m_j\right) + v\,m_j\,d\ln\left(\gamma_\pm\right) = 0$$

Then,

$$-\phi\,dm_j - m_j\,d\phi + v\,dm_j + v\,m_j\,d\ln\left(\gamma_\pm\right) = 0$$

$$v\,m_j\,d\ln\left(\gamma_\pm\right) = \phi\,dm_j - v\,dm_j + m_j\,d\phi$$

Or,

$$\mathrm{d\ln\left(\gamma_\pm\right) = (\phi - v)\,\frac{dm_j}{v\,m_j} + \frac{d\phi}{v}}$$

For a solute where one mole of pure solute forms one mole of solute in solution,

$$\mathrm{d\ln\left(\gamma\right) = (\phi - 1)\,\frac{dm_j}{m_j} + d\phi}$$

Then,

$$\ln(\gamma) = (\phi - 1)\ + \int_0^{\mathrm{m(j)}} (\phi - 1)\,\mathrm{d\ln\left(m_j\right)}$$

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1.11.3: Gibbs-Duhem Equation- Solvent and Solutes- Aqueous Solutions

A given aqueous solution at temperature T and pressure p (which is close to the standard pressure) is prepared using water ($1\ \mathrm{kg}$) and $\mathrm{m_j}$ moles of solute-j. The chemical potential of solute–j is given by equation (a) where $\mu_{\mathrm{j}}^{0}(\mathrm{aq})$ is the chemical potential of solute-j in an aqueous solutions where $\mathrm{m_j} = 1\ \mathrm{molkg^{-1}}$ and the thermodynamic properties of the solution are ideal.

$$\mu_{\mathrm{j}}(\mathrm{aq}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\,ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right)$$

At all T and p,

$$\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\gamma_{\mathrm{j}} = 1$$

The chemical potential of solvent, water $\mu_1(\mathrm{aq})$ is given by equation (c) where $\mu_1^{*}(\ell)$ is the chemical potential of water(ℓ) at the same T and p; ϕ is the molal osmotic coefficient.

$$\mu_1(\mathrm{aq}) = \mu_1^{*}(\ell) - \phi\,\mathrm{R\,T\,M_1\,m_j}$$

At all T and p,

$$\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\phi = 1$$

For a solution at fixed T and p, the Gibbs-Duhem equation relates $\mu_1(\mathrm{aq})$ and $\mu_{\mathrm{j}}(\mathrm{aq})$ using equation (e).

$$(1/\mathrm{M_1})\ \mathrm{d}\mu_1(\mathrm{aq}) + \mathrm{m_j}\,\mathrm{d}\mu_{\mathrm{j}}(\mathrm{aq}) = 0$$

Therefore

$$\begin{aligned}&(1/\mathrm{M_1})\ \mathrm{d}\left[\mu_1^{*}(\ell) - \phi\,\mathrm{R\,T\,M_1\,m_j}\right]\\&+\mathrm{m_j\,d}\left[\mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right)\right] = 0\end{aligned}$$

Thus,

$$\mathrm{d}\left(-\phi\,\mathrm{m_j}\right) + \mathrm{m_j\,d\,ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}\right) = 0$$

$$-\phi\,dm_j - m_j\,d\phi + m_j\,d\ln\left(m_j\right) + m_j\,d\ln\left(\gamma_j\right) = 0$$

From equation (h) (dividing by $\mathrm{m_j}$)

$$-\phi\,d\ln\left(m_j\right) - d\phi + d\ln\left(m_j\right) + d\ln\left(\gamma_j\right) = 0$$

$$\mathrm{d\ln}\left(\gamma_{\mathrm{j}}\right) = \mathrm{d}\phi - (1-\phi)\,\mathrm{d\ln}\left(\mathrm{m_j}\right)$$

The latter equation is integrated between the limits '$\mathrm{m_j} = 0$' and $\mathrm{m_j}$; equivalent to limits '$\phi = 1$' and ϕ.

$$\int_0^{m(j)} d\ln\left(\gamma_j\right) = \int_{\phi=1}^{\phi} \mathrm{d}\phi - \int_0^{m(j)} (1-\phi)\,d\ln\left(m_j\right)$$

Then,

$$-\ln\left(\gamma_{\mathrm{j}}\right) = (1-\phi) + \int_0^{\mathrm{m(j)}} (1-\phi)\,\mathrm{d\ln}\left(\mathrm{m_j}\right)$$

From equation (g)

$$\mathrm{d}\left[\phi\,\mathrm{m_j}\right] = \mathrm{m_j\,d}\left[\ln\left(\mathrm{m_j}/\mathrm{m}^{0}\right)\right] + \mathrm{m_j\,d}\left[\ln\left(\gamma_{\mathrm{j}}\right)\right]$$

or,

$$\mathrm{d}\left[\phi\,\mathrm{m_j}\right] = \mathrm{m}^{0}\,\mathrm{d}\left[\mathrm{m_j}/\mathrm{m}^{0}\right] + \mathrm{m_j\,d}\left[\ln\left(\gamma_{\mathrm{j}}\right)\right]$$

Following integration from '$\mathrm{m_j} = 0$' to $\mathrm{m_j}$,

$$\phi\,\mathrm{m_j} = \mathrm{m_j} + \int_0^{\mathrm{m_j}} \mathrm{m_j\,d\ln}\left(\gamma_{\mathrm{j}}\right)$$

or,

$$\phi = 1 + (1/\mathrm{m_j}) \int_0^{\mathrm{m_j}} \mathrm{m_j}\, \mathrm{d} \ln (\gamma_\mathrm{j})$$

Hence,

$$\phi - 1 = (1/\mathrm{m_j}) \int_0^{\mathrm{m_j}} \mathrm{m_j}\, \mathrm{d} \ln (\gamma_\mathrm{j})$$

In other words, $(\phi - 1)$ is related to the integral of $\mathrm{m_j}\, \mathrm{d} \ln \gamma_\mathrm{j}$ between the limits '$\mathrm{m_j} = 0$' and $\mathrm{m_j}$. Equation (q) marks the limit of the thermodynamics analysis. However we explore the significance of the equation by adopting an equation relating ϕ and $\mathrm{m_j}$. Equation (r) signals one assumption in which r is a parameter characteristic of the solution under examination. Thus

$$\phi - 1 = \alpha\ (\mathrm{m_j})^\mathrm{r}$$

Then [1]

$$-\ln (\gamma_\mathrm{j}) = (1 - \phi)\, (1 + \mathrm{r})/\mathrm{r}$$

Or,

$$(1 - \phi) = [r/(1 + r)]\ \{-\ln (\gamma_j)\}$$

From equation (m),

$$\phi = 1 - \alpha\ (\mathrm{m_j})^\mathrm{r}$$

If for example, $\alpha > 1$, then $\phi < 1$ for all solutions. According to equation (c),

$$\mu_1(\mathrm{aq}) - \mu_1^*(\ell) = -\left[1 - \alpha\ (\mathrm{m_j})^\mathrm{t}\right]\ \mathrm{R\,T\,M_1\,m_j}$$

If therefore $\phi > 1, \mu_1(\mathrm{aq}) < \mu_1^*(\ell)$; relative to the chemical potential of the pure solvent, the solvent in the solution is stabilised. For the solute according to equation (n),

$$-\ln (\gamma_\mathrm{j}) = [(1 + \mathrm{r})/\mathrm{r}]\ [\alpha\ (\mathrm{m_j})^\mathrm{r}]$$

Or, [Bjerrum's Equation]

$$-\ln (\gamma_\mathrm{j}) = [(1 + \mathrm{r})/\mathrm{r}]\, [1 - \phi]$$

Footnotes

[1] From equations (q) and (s),

$$-\ln (\gamma_\mathrm{j}) = \alpha\ (\mathrm{m_j})^\mathrm{r} + \alpha \int_0^{\mathrm{m(j)}} (\mathrm{m_j})^{\mathrm{r}-1}\ d\ \mathrm{m_j}$$

Then,

$$\begin{aligned} -\ln (\gamma_\mathrm{j}) &= \alpha\ (\mathrm{m_j})^\mathrm{r} + \alpha\ (\mathrm{m_j})^\mathrm{r}/\mathrm{r} \\ &= \alpha\ (\mathrm{m_j})^\mathrm{r}\ [1 + (1/\mathrm{r})] \end{aligned}$$

Hence, $-\ln (\gamma_\mathrm{j}) = \alpha\ (\mathrm{m_j})^\mathrm{r}\ [1 + \mathrm{r}]/\mathrm{r}$

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1.11.4: Gibbs-Duhem Equation- Aqueous Salt Solutions- Salt and Solvent- Debye-Huckel Limiting Law

A given aqueous salt solution at temperature T and pressure p (which is close to the standard pressure) is prepared using water ($1\ \mathrm{kg}$) and $\mathrm{m_j}$ moles of a 1:1 sa }\) and the thermodynamic properties of the solution are ideal.

$$\mu_{\mathrm{j}}(\mathrm{aq}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + 2\,\mathrm{R\,T}\,\ln\left(\mathrm{m_j}\,\gamma_{\pm}/\mathrm{m}^{0}\right)$$

At all T and p,

$$\text{limit}\,(\mathrm{m_j} \rightarrow 0)\,\gamma_{\pm} = 1$$

The chemical potential of solvent, water $\mu_1(\mathrm{aq})$ is related to salt molality $\mathrm{m_j}$ by equation (c) where $\mu_1^{*}(\ell)$ is the chemical potential of water(ℓ) at the same T and p and ϕ is the molal osmotic coefficient.

$$\mu_1(\mathrm{aq}) = \mu_1^{*}(\ell) - 2\,\phi\,\mathrm{R\,T\,M_1\,m_j}$$

At all T and p,

\[\operatorname{limit}\left(\mathrm{m}_{\mathrm{j}} \rightarrow 0\right) \phi=1\)

For a solution at fixed T and p, the Gibbs-Duhem equation relates $\mu_1(\mathrm{aq})$ and $\mu_j(\mathrm{aq})$ using equation (e).

$$(1/M_1)\ d\mu_1(aq) + m_j\,d\mu_j(aq) = 0$$

Therefore

$$\begin{aligned}&(1/\mathrm{M_1})\ \mathrm{d}\left[\mu_1^{*}(\ell) - 2\,\phi\,\mathrm{R\,T\,M_1\,m_j}\right]\\ &+\mathrm{m_j\,d}\left[\mu_{\mathrm{j}}^{0}(\mathrm{aq}) + 2\,\mathrm{R\,T}\,\ln\left(\mathrm{m_j}\,\gamma_{\pm}/\mathrm{m}^{0}\right)\right] = 0\end{aligned}$$

$$\mathrm{d}\left(-\phi\,\mathrm{m_j}\right) + \mathrm{m_j\,d\ln}\left(\mathrm{m_j}\,\gamma_{\pm}\right) = 0$$

At '$\mathrm{m_j} = 0$', ϕ is unity. Therefore integration [1] of equation (g) yields equation (h)

$$\phi = 1 + \frac{1}{m_j}\int_0^{m(j)} m_j\,d\ln\left(\gamma_{\pm}\right)$$

We have an equation for ϕ in terms of $\mathrm{m_j}$ and $\gamma_{\pm}$. Equation (h) signals the limit of the thermodynamic analysis. To make progress we need an equation for $\gamma_{\pm}$ in terms of $\mathrm{m_j}$. The Debye-Huckel Limiting Law provides such an equation having the form shown in equation (i) where S_{γ} is positive and a function of temperature, pressure and relative permittivity of the solvent. Thus

$$\ln\left(\gamma_{\pm}\right) = -S_{\gamma}\ \left(m_j/m^{0}\right)^{1/2}$$

From equation (h),

$$\phi = 1 - \frac{S_{\gamma}}{\left(m^{0}\right)^{1/2}\ m_j}\int_0^{m(j)} m_j\,d\left(m_j\right)^{1/2}$$

Hence [2],

\[\phi=1-\left(\mathrm{S}_{\gamma} / 3\right) \,\left(\mathrm{m}_{\mathrm{j}} / \mathrm{m}^{0}\right)^{1 / 2}\)

We examine the impact of equations (i) and (k) on the chemical potentials of solute and solvent. From equation (c),

$$\mu_1(\mathrm{aq}) - \mu_1^{*}(\ell) = -2\,\mathrm{R\,T\,M_1\,m_j}\ \left[1 - \left(\mathrm{S}_{\gamma}/3\right)\ \left(\mathrm{m_j}/\mathrm{m}^{0}\right)^{1/2}\right]$$

For a salt solution having thermodynamic properties which are ideal,

$$\mu_1(\mathrm{aq;id}) - \mu_1^{*}(\ell) = -2\,\mathrm{R\,T\,M_1\,m_j}$$

Then,

$$\mu_1(\mathrm{aq}) - \mu_1(\mathrm{aq;id}) = 2\,\mathrm{R\,T\,M_1}\ \left(\mathrm{S}_{\gamma}/3\right)\ \left(\mathrm{m}^{0}\right)^{-1/2}\ \left(\mathrm{m_j}\right)^{3/2}$$

But S_γ is positive. Hence $[\mu_1(aq) - \mu_1(aq; id)]$ is positive so that in terms of the DHLL the chemical potential of water is raised above that in the corresponding solution having ideal thermodynamic properties.

For the solute, equation (a) requires that $\mu_j(aq)$ is given by equation (o).

$$\mu_j(aq) = \mu_j^0(aq) + 2\,R\,T\,\ln\left(m_j/m^0\right) + 2\,R\,T\,\ln\left(\gamma_\pm\right)$$

Or,

$$\mu_j(aq; id) = \mu_j^0(aq) + 2\,R\,T\,\ln\left(m_j/m^0\right)$$

Then using equation (i),

$$\mu_j(aq) - \mu_j(aq; id) = -2\,R\,T\,S_\gamma\,\left(m_j/m^0\right)^{1/2}$$

According therefore to the DHLL, salt j in a real solution is stabilised relative to that in an ideal solution. In other words according to the DHLL the salt is stabilised whereas the solvent is destabilised, the impact of ion-ion interactions on the Gibbs energy of a solution is moderated.

Footnotes

[1] $-\phi\,dm_j - m_j\,d\phi + m_j\,d\left[\ln\left(m_j\right)\right] + m_j\,d\ln\left(\gamma_\pm\right) = 0$
$-\phi\,dm_j - m_j\,d\phi + \left(m_j/m_j\right)\,dmm_j + m_j\,d\ln\left(\gamma_\pm\right) = 0$

Then, $-(\phi - 1)\,dm_j - m_j\,d\phi + m_j\,d\ln\left(\gamma_\pm\right) = 0$

Hence, $-\int_0^{m(j)}(\phi - 1)\,dm_j - \int_0^{m(j)} m_j\,d\phi = -\int_0^{m(j)} m_j\,d\ln\left(\gamma_\pm\right)$

Or, $\phi = 1 + \frac{1}{m_j}\int_0^{m(j)} m_j\,d\ln\left(\gamma_\pm\right)$

[2] Put $(m_j)^{1/2} = x$; $\int_0^{m(j)} x^2\,dx = x^3/3 = (m_j)^{3/2}/3$

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1.12: Expansions

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1.12.1: Heat Capacities- Isobaric- Solutions

From the definition of enthalpy H, an infinitesimal small change in enthalpy is related to the corresponding change in thermodynamic energy dU by equation (a).

$$\mathrm{dH} = \mathrm{dU} + \mathrm{p}\,\mathrm{dV} + \mathrm{V}\,\mathrm{dp}$$

If only '$\mathrm{p-V}$' work is involved,

$$\mathrm{dU} = \mathrm{q} - \mathrm{p}\,\mathrm{dV}$$

Then

$$\mathrm{dH} = \mathrm{q} + \mathrm{V}\,\mathrm{dp}$$

But in general terms,

$$\mathrm{q} = \mathrm{C}\,\mathrm{dT}$$

Here C is the heat capacity of the system, an extensive variable. Hence for a change at constant pressure,

$$\mathrm{dH} = \mathrm{C_p}\,\mathrm{dT}$$

Isobaric heat capacity is related to the change in enthalpy accompanying a change in temperature.

$$\mathrm{C}_p = (\partial \mathrm{H}/\partial \mathrm{T})_\mathrm{p}$$

$\mathrm{C_p}$ is an extensive variable; $\mathrm{C_{pm}}$ is the corresponding molar property. We develop the above analysis in a slightly different way in order to make an important point. We explore the relationship between the dependence of $(\mathrm{G/T})$ on temperature at

i. constant affinity and
ii. constant extent of reaction.

A calculus operation yields the following equation.

$$\left[\frac{\partial(\mathrm{G/T})}{\partial \mathrm{T}}\right]_{\mathrm{p,A}} = \left[\frac{\partial(\mathrm{G/T})}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi} - \frac{1}{\mathrm{T}}\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{T,p}}\left[\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}\left[\frac{\partial \mathrm{G}}{\partial \xi}\right]_{\mathrm{T,p}}$$

But at equilibrium,

$$A = -\left[\frac{\partial G}{\partial \xi}\right]_{\mathrm{T,p}} = 0$$

Using the Gibbs-Helmholtz Equation,

$$\mathrm{H(A=0)} = \mathrm{H}\,(\xi^{\mathrm{eq}})$$

This result is expected because enthalpy H is a strong state variable, a function of state which does not need a description of a pathway. This is not the case for isobaric heat capacities. Using the same calculus operation,

$$\left[\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right]_{\mathrm{p,A}} = \left[\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi} - \left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{T,p}}\left[\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}\left[\frac{\partial \mathrm{H}}{\partial \xi}\right]_{\mathrm{T,p}}$$

We cannot assume that the triple product term is zero. Hence there are two limiting isobaric heat capacities; the equilibrium isobaric heat capacity, $\mathrm{C_p(A=0)}$ and the 'frozen' isobaric heat capacity, \(\mathrm{C}_\mathrm{p}\left(\xi_\mathrm{eq}\right)\).

$$\mathrm{C_p(A=0)} = \mathrm{C_p}\,(\xi^{\mathrm{eq}}) - \left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{T,p}}\left[\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}\left[\frac{\partial \mathrm{H}}{\partial \xi}\right]_{\mathrm{T,p}}$$

In other words, the isobaric heat capacity is not a strong function of state. The property is concerned with a pathway between states. The term \left[-\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{T}, \mathrm{p}} \,\left[\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right]_{\mathrm{p}, \xi} \,\left[\frac{\partial \mathrm{H}}{\partial \xi}\right]_{\mathrm{T}, \mathrm{p}}\right]\) is the relaxational isobaric heat capacity. $\mathrm{C_p(A=0)}$, the equilibrium heat capacity, signals that when heat q

passes into a system, the composition - organization of the system changes in order that the Gibbs energy of the system remains at a minimum. In contrast $C_p\,(\xi_{eq})$, the frozen heat capacity, signals that no changes occur in the composition – organization in the system such that the Gibbs energy is displaced from the original minimum. Moreover the equilibrium isobaric heat capacity is always larger than the frozen isobaric heat capacity. Indeed we can often treat the extensive equilibrium property $C_p(A = 0)$ as a function of state.

Certainly isobaric heat capacities differentiate water as a solvent from other associated liquids [1,2] such as H_2O_2, and N_2H_4 and low melting fused salts such as ethylammonium nitrate. Interestingly, among liquids, water has one of the highest heat capacitances; i.e. heat capacities per unit volume [3]. Therefore hypothermia is often life threatening for babies and old persons because in order to raise their temperature a large amount of thermal energy has to be passed into the body in order to raise their temperature. This is often difficult without damaging the skin and other body tissues--- a consequence of humans being effectively concentrated aqueous systems.

The isobaric heat capacity of a solution prepared using n_1 moles of solvent (water) and n_j moles of solute j at temperature T and pressure p is defined by equation (1).

$$C_p = C_p\,[T, p, n_1, n_j]$$

We assume the system is at thermodynamic equilibrium such that the affinity for spontaneous change is zero at a minimum in Gibbs energy. The isobaric heat capacity of the solution is related to the composition using equation (m).

$$C_p(aq) = n_1\,C_{p1}(aq) + n_j\,C_{pj}(aq)$$

Here $C_{p1}(aq)$ and $C_{pj}(aq)$ are the partial molar isobaric heat capacities enthalpies of solvent and solute respectively. Alternatively $C_p(aq)$ is given by equation (n) where $C^*_{p1}(\ell)$ and $\phi\,(C_{pj})$ are the molar isobaric heat capacity of the pure solvent and the apparent molar isobaric heat capacity of the solute j respectively. Thus

$$C_p(aq) = n_1\,C^*_{p1}(\ell) + n_j\,\phi\,(C_{pj})$$

Footnotes

[1] M. Allen, D. F. Evans and R. Lumry, J. Solution Chem.,1985,**14**,549.

[2] M. Hadded, M. Biquard, P. Letellier and R. Schaal, Can. J. Chem.,1985,**63**,565.

[3]

Liquid	Heat Capacitance $C_p/\ JK^{-1}\ cm^{-3}$
Water	4.18
Propane	1.67
Cyanomethane	2.26
Ethanol	1.92
Tetrachloroethane	1.38

See J. K. Grime, in Analytical Solution Calorimetry, ed. J. K.Grime, Wiley, New York, 1985, chapter 1.

For isochoric and isobaric heat capacities of liquids see, D. Harrison and E. A. Moelwyn-Hughes, Proc. R. Soc. London, Ser.A,1957, **239**, 230.

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1.12.2: Heat Capacity- Isobaric- Partial Molar- Solution

Equilibrium isobaric heat capacities of solutions can be treated for most purposes as extensive variables. Thus for an aqueous solution prepared using $\mathrm{n_1}$ moles of solvent (water) and $\mathrm{n_j}$ moles of a simple solute j the isobaric (equilibrium) heat capacity of the solution $\mathrm{C_p(aq)}$ can be related to the composition of the solution using equations (a) and (b) [1].

$$\mathrm{C_p(aq;A=0) = n_1\,C_{p1}(aq) + n_j\,C_{pj}(aq)}$$

where

$$\mathrm{C_{pl}(aq) = \left(\frac{\partial C_p(aq;A=0)}{\partial n_1}\right)_{T,p,n(j)} \quad \text{and } C_{pj}(aq) = \left(\frac{\partial C_p(aq;A=0)}{\partial n_j}\right)_{T,p,n(l)}}$$

Similar equations are encountered in a discussion of the partial molar enthalpies but with reference to these properties we develop a number of strategies because it is not possible to determine the enthalpy of a solution. In the present case the outlook is much more favourable because it is possible to measure isobaric heat capacities of solutions [1-3]. The fact that we can measure the temperature dependence of the equilibrium enthalpy of a solution but not the actual enthalpy is an interesting philosophical point. Nevertheless it is informative to develop the analysis starting from equations relating partial molar enthalpies and compositions of solutions.

A given aqueous solution is prepared using $\mathrm{n_1}$ moles of solvent (water) and $\mathrm{n_j}$ moles of solute. The partial molar enthalpies are related to the composition of the solution by the following equations. Thus

$$\mathrm{H_1(aq) = H_1^*(\ell) + R\,T^2\,M_1\,m_j\,(\partial\phi/\partial T)_p}$$

and

$$\mathrm{H_j(aq) = H_j^\infty(aq) - R\,T^2\,[\partial \ln(\gamma_j)/\partial T)_p}$$

At all T and p,

$$\mathrm{limit}\,(m_j \to 0)\,\phi = 1 \text{ and } \gamma_j = 1$$

By definition,

$$\mathrm{C_{p1}(aq) = \left(\frac{\partial C_p}{\partial n_1}\right)_{T,p,n(j)} = \left(\frac{\partial H_1}{\partial T}\right)_p = \left(\frac{\partial^2 H}{\partial n_1\,\partial T}\right)_{p,n(j)}}$$

And,

$$\mathrm{C_{pj}(aq) = \left(\frac{\partial C_p}{\partial n_j}\right)_{T,p,n(1)} = \left(\frac{\partial H_j}{\partial T}\right)_p = \left(\frac{\partial^2 H}{\partial n_j\,\partial T}\right)_{p,n(1)}}$$

The latter two equations trace the story from the enthalpy of the solution to partial molar isobaric heat capacities. Using equation (f) in conjunction with equation (c) we obtain an equation for dependence for $\mathrm{C_{p1}(aq)}$ on molality $\mathrm{m_j}$.

$$\mathrm{C_{pl1}(aq) = C_{pl1}^*(\ell) + 2\,R\,T\,M_1\,m_j\,(\partial\phi/\partial T)_p + R\,T^2\,M_1\,m_j\,\left(\partial^2\phi/\partial T^2\right)_p}$$

Similarly using equations (d) and (g), we obtain an equation relating $\mathrm{C_{pj}(aq)}$ and molality $\mathrm{m_j}$; the origin of the two minus signs is the Gibbs - Helmholtz Equation.

$$\mathrm{C_{pj}(aq) = C_{pj}^\infty(aq) - 2\,R\,T\,[\partial \ln(\gamma_j)/\partial T]_p - R\,T^2\,\left[\partial^2 \ln(\gamma_j)/\partial T^2\right]_p}$$

We consider a solution prepared using $1\ \mathrm{kg}$ of water and $\mathrm{m_j}$ moles of solute j [4].

$$\mathrm{C_p\,(aq;w_1 = 1\ kg) = (1/M_1)\ C_{pl}(aq) + m_j\,C_{pj}\ (aq)}$$

If the thermodynamic properties of the solution are ideal, from the definitions of both practical osmotic coefficient ϕ and activity coefficient γ_j, the last two terms in equations (h) and (i) are zero.

$$\mathrm{C_p\,(aq;id;w_1 = 1\ kg) = (1/M_1)\ C_{p1}^*(\ell) + m_j\,C_{pj}^\infty(aq)}$$

This is an interesting equation because two experiments yield $C_p(aq; id)$ and $C^*_{p1}(\ell)$. Hence, granted the ideal conditions, we obtain an estimate of $C^\infty_{pj}(aq)$, limiting isobaric heat capacity of solute j in solution. Unfortunately the assumption concerning ideal properties of a solution is often unrealistic. Nevertheless equation (k) offers a reference against which we can examine the properties of real solutions.

Footnotes

[1] An important technological development was the design of the Picker flow calorimeter; P. Picker, P.-A. Leduc, P. R. Philip and J. E. Desnoyers, J. Chem. Thermodyn.,1971, **3**,631.

[2] For details of calibration of the Picker calorimeter; D. E.White and R. H. Ward, J. Solution Chem.,1982,**11**,223.

[3] For extension to measurement of thermal expansion coefficients; J. F. Alary, M. N. Simard, J. Dumont and C. Jolicoeur, J. Solution Chem.,1982,**11**,755.

[4] $\left[\mathrm{JK^{-1}\ kg^{-1}}\right] = \left[\mathrm{kg\,mol^{-1}}\right]^{-1}\ \left[\mathrm{JK^{-1}\ mol^{-1}}\right] + \left[\mathrm{mol\ kg^{-1}}\right]\ \left[\mathrm{JK^{-1}\ mol^{-1}}\right]$

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1.12.3: Heat Capacities- Isobaric and Isochoric

When heat q passes smoothly (reversibly) into a closed system from the surroundings, the temperature of the system increases (if there are no phase changes, e.g. liquid to vapour). The increase in temperature $\Delta \mathrm{T}$ is related to heat q using equation (a).

$$\mathrm{q} = \mathrm{C}\,\Delta \mathrm{T}$$

Heat capacity C is an extensive property of a system whereas $\Delta \mathrm{T}$ is the change in an intensive variable. For a given amount of heat, a more dramatic increase in temperature is produced the lower is the heat capacity C. Moreover as defined by equation (a) the heat capacity of a system is not a thermodynamic function of state because heat capacity describes a pathway accompanying a change in temperature. Hence, we define precisely the pathway taken by the system. Two important classes of heat capacities are

i. isobaric, $\mathrm{C_p}$, and
ii. isochoric, CV.

Isochoric and isobaric heat capacities are related to the isobaric expansions $\mathrm{E_p}$ and isothermal compression KT using equation (b) [1].

$$\mathrm{C_V} = \mathrm{C_p} - \mathrm{T}\,(\mathrm{E_p})^2/\mathrm{K_T}$$

Heat capacities and compressions are simply related [2].

$$\mathrm{K_T}/\mathrm{K_S} = \mathrm{C_p}/\mathrm{C_V}$$

Footnotes

[1] According to a calculus operation, the dependences of entropy on temperature at constant volume and constant pressure are related. $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{p}} - \left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{T}} \left(\frac{\partial \mathrm{p}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$ A Maxwell equation requires that $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ Hence,

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{p}} + \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}} \left(\frac{\partial \mathrm{p}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

But the isobaric expansion, $E_p = \left(\frac{\partial V}{\partial T}\right)_p$ And the isothermal compression, $\mathrm{K_T} = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$ From the Gibbs –Helmholtz equation, $\mathrm{C_V} = \mathrm{T}\,\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$ And $C_p = T\,\left(\frac{\partial S}{\partial T}\right)_p$ Then

$$C_V = C_p - T\,(E_p)^2/K_T$$

The latter equation is correct under the condition of either ‘at constant affinity A’ or ‘at constant composition’.

[2] The starting point is the following equation.

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = -\left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{V}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}} = -\left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{V}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{p}} \left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$
$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{S}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{V}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{p}} = -\left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{v}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{p}} \left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

Then $(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T}}/(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{S}} = (\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{p}}/(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{V}}$ Hence,

$$\mathrm{K_T}/\mathrm{K_S} = \mathrm{C_p}/\mathrm{C_V}$$

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1.12.4: Heat Capacities- Isobaric- Equilibrium and Frozen

An aqueous solution is prepared using n_1 moles of water(ℓ) and n_j moles of solute at temperature T and pressure p. The system is at equilibrium where the affinity for spontaneous change is zero. Hence,

$$\mathrm{H}^{\mathrm{eq}} = \mathrm{H}^{\mathrm{eq}}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}, \mathrm{A} = 0, \xi^{\mathrm{eq}}\right]$$

Heat capacities describe a pathway. There are two limiting pathways. The system can be displaced either to a nearby state along a pathway for which ξ is constant or along a pathway for which the affinity for spontaneous change is constant. The accompanying differential changes in enthalpies are unlikely to be the same. In fact they are related using a calculus procedure.

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{A,p}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\xi,\mathrm{p}} - \left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\xi,\mathrm{p}} \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}} \left(\frac{\partial \mathrm{H}}{\partial \xi}\right)_{\mathrm{T,p}}$$

If the original state was an equilibrium state we write this equation in the following form which incorporates an equation for the dependence of affinity A on temperature at equilibrium.

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{A=0,p}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\xi\mathrm{eq,p}} - \frac{1}{\mathrm{T}}\left[\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)^{\mathrm{eq}}_{\mathrm{T,p}}\right]^2 \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)^{\mathrm{eq}}_{\mathrm{T,p}}$$

Then from the definition of isobaric heat capacity [1],

$$\mathrm{C_p}(\mathrm{A} = 0) = \mathrm{C_p}\left(\xi^{\mathrm{eq}}\right) - \frac{1}{\mathrm{T}}\left[\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)^{\mathrm{eq}}_{\mathrm{T,p}}\right]^2 \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)^{\mathrm{eq}}_{\mathrm{T,p}}$$

Here $(\partial \mathrm{H}/\partial \xi)^{\mathrm{eq}}_{\mathrm{T,p}}$, is the enthalpy of reaction. For a stable equilibrium state $(\partial \mathrm{A}/\partial \xi)^{\mathrm{eq}}_{\mathrm{T,p}}$, is negative. Hence,

$$\mathrm{C_p}(\mathrm{A} = 0) > \mathrm{C_p}\left(\xi^{\mathrm{eq}}\right)$$

Here $\mathrm{C_p}(\mathrm{A} = 0)$ is the equilibrium heat capacity signalling that when heat q passes into the system the composition/organisation of the system changes in order that the Gibbs energy of the system remains at a minimum. In contrast $\mathrm{C_p}\left(\xi^{\mathrm{eq}}\right)$ is the frozen capacity signalling that no changes occur in the composition/organisation in the system such that the Gibbs energy of the system is displaced from the original minimum. Moreover, equation (e) shows that the equilibrium isobaric heat capacity is always larger than the frozen isobaric heat capacity. Indeed we can often treat the extensive equilibrium property $\mathrm{C_p}(\mathrm{A} = 0)$ as a function of state (although it is not).

Footnote

[1] $\frac{1}{T}\left[\left(\frac{\partial \mathrm{H}}{\partial \xi}\right)^{\mathrm{eq}}_{\mathrm{T,p}}\right]^2 \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}} = \frac{1}{[\mathrm{K}]}\left[\frac{\mathrm{J}}{\mathrm{mol}}\right]^2 \left[\frac{\mathrm{mol}}{\mathrm{Jmol}^{-1}}\right] = [\mathrm{JK}^{-1}]$

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1.12.5: Heat Capacity- Isobaric- Solutions- Excess

A given solution is prepared using $1\ \mathrm{kg}$ of solvent (water) and m_j moles of solute j. If the thermodynamic properties of this solution are ideal, the isobaric heat capacity can be expressed as follows [1].

$$\mathrm{C_p\,(aq; id; w_1 = 1\ kg) = (1/M_1)\ C^*_{p1}(\ell) + m_j\, C^\infty_{pj}(aq)}$$

On the other hand for a real solution the isobaric heat capacity can be expressed in terms of the apparent molar heat capacity of the solute, $\phi\,(\mathrm{C_{pj}})$.

$$\mathrm{C_p\,(aq; w_1 = 1\ kg) = (1/M_1)\ C^*_{p1}(\ell) + m_j\, \phi\,(C_{pj})}$$

The difference between $\mathrm{C_p\,(aq; w_1 = 1\ kg)}$ and $\mathrm{C_p\,(aq; id; w_1 = 1\ kg)}$ defines the relative isobaric heat capacity of the solution J, an excess property.

$$\mathrm{J(aq) = C_p\,(aq; w_1 = 1\ kg) - C_p\,(aq; id; w_1 = 1\ kg)}$$

Thermodynamics does not define the magnitude or sign of $\mathrm{J(aq)}$. However, from the definitions of ideal and real partial molar isobaric capacities of solvent and solute, the following condition must hold.

$$\mathrm{limit\,(m_j \to 0)\,J(aq) = 0}$$

Relative quantities can also be defined for solute and solvent.

$$\mathrm{J_j(aq) = C_{pj}(aq) - C^\infty_{pj}(aq)}$$

$$\mathrm{J_1(aq) = C_{p1}(aq) - C^*_{p1}(\ell)}$$

Also,

$$\mathrm{\phi\,(J_j) = \phi\,[C_{pj}(aq)] - C^\infty_{pj}(aq)}$$

Hence,

$$\mathrm{limit\,(m_j \to 0)\,J_j(aq) = J_1(aq) = \phi\,(J_j) = 0}$$

Equation (c) defines a property J which is an excess isobaric heat capacity of a solution prepared using $1\ \mathrm{kg}$ of water. Thus,

$$\mathrm{C^E_p\,(aq; w_1 = 1\ kg) = J(aq) = C_p\,(aq; w_1 = 1\ kg) - C_p\,(aq; id; w_1 = 1\ kg)}$$

From equations (a) and (b),

$$\mathrm{C^E_p\,(aq; w_1 = 1\ kg) = m_j\ [\phi\,(C_{pj}) - C^\infty_{pj}(aq)]}$$

From equation (g),

$$\mathrm{C^E_p\,(aq; w_1 = 1\ kg) = m_j\,\phi\,(J_j)}$$

Thus $\phi\,(\mathrm{J}_j)$ is the relative apparent molar isobaric heat capacity of the solute in a given real solution. Isobaric heat capacities of solutions and related partial molar isobaric heat capacities reflect in characteristic fashion the impact of added solutes on water water interactions

Footnote

[1] $\mathrm{[JK^{-1}\ kg^{-1}] = [kgmol^{-1}]^{-1}\ [JK^{-1}\ mol^{-1}] + [molkg^{-1}]\ [JK^{-1}\ mol^{-1}]}$

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1.12.6: Heat Capacities- Isobaric- Dependence on Temperature

Interesting cases emerge where an equilibrium isobaric heat capacity reflects a change in composition as a consequence of the system changing composition in order to hold the system at equilibrium. The development of sensitive scanning calorimeters stimulated research in this subject [1], particularly with respect to biochemical research [2]; e.g. multilamellar systems [3].

We consider the case where a solution is prepared using $\mathrm{n_1}$ moles of water and $\mathrm{n_x}$ moles of solute X. In solution at temperature T (and fixed pressure p) the following chemical equilibrium is established.

	$\mathrm{X(aq) \Longrightarrow Y(aq)}$		
At equilibirum	$\mathrm{n_x^0 - \xi}$	ξ	moles
or,	$\mathrm{n_x^0\,\left[1 - \frac{\xi}{n_x^0}\right]}$	$\mathrm{n_x^0\,\left[\frac{\xi}{n_x^0}\right]}$	moles

By definition $\alpha = \xi/\mathrm{n_x^0}$, the degree of reaction forming substance Y at equilibrium. Then $\mathrm{n_x^{eq} = n_x^0\,(1-\alpha)}$ and $\mathrm{n_y^{eq} = \alpha\,n_x^0}$.

If $\mathrm{w_1}$ is the mass of solvent, water(ℓ), the equilibrium molalities are $\mathrm{m_x^0\,(1-\alpha)}$ for chemical substance X and $\alpha\,\mathrm{m_x^0}$ for chemical substance Y. For the purposes of the arguments advanced here we assume that the thermodynamic properties of the solution are ideal. The equilibrium composition of the closed system at defined temperature and pressure is described by the equilibrium constant $\mathrm{K^0}$. Then,

$$\mathrm{K^0} = \alpha/(1-\alpha)$$

Hence the (dimensionless and intensive) degree of reaction,

$$\alpha = \mathrm{K^0}/\left(1+\mathrm{K^0}\right)$$

Because $\mathrm{K^0}$ is dependent on temperature then so is the degree of reaction. The extent to which an increase in temperature favours or disfavours formation of more $\mathrm{Y(aq)}$ depends on the sign of the enthalpy of reaction, $\Delta_r\mathrm{H^0}$. Thus [4,5],

$$\frac{\mathrm{d}\alpha}{\mathrm{dT}} = \frac{\mathrm{K^0}}{\left(1+\mathrm{K^0}\right)^2}\left[\frac{\mathrm{d\ln K^0}}{\mathrm{dT}}\right]$$

The analysis at this point is considerably simplified if we assume that the limiting enthalpy of reaction, $\Delta_r\mathrm{H^\infty(aq)}$ for the chemical reaction is independent of temperature (at pressure p). Hence using the van't Hoff equation,

$$\frac{\mathrm{d}\alpha}{\mathrm{dT}} = \frac{1}{\mathrm{R\,T^2}}\,\frac{\mathrm{K^0}}{(1+\mathrm{K^0})}\,\Delta_\mathrm{r}\mathrm{H^\infty(aq)}$$

Thus the shift in the composition of the solution depends on the sign of the limiting enthalpy of reaction. If $\Delta_\mathrm{r}\mathrm{H^\infty(aq)} < 0$, an increase in temperature favours an increase in the amount of $\mathrm{X(aq)}$ at the expense of $\mathrm{Y(aq)}$. At temperature T, the enthalpy of the solution is given by equation (e) where $\mathrm{H_1^*(\ell)}$ is the molar enthalpy of the solvent.

$$\mathrm{H(aq;\,A=0) = n_1\,H_1^*(\ell) + n_x^0\,(1-\alpha)\,H_x^\infty(aq) + n_x^0\,\alpha\,H_y^\infty(aq)}$$

or,

$$\mathrm{H(aq;\,A=0) = n_1\,H_1^*(\ell) + n_x^0\,H_x^\infty(aq) + \alpha\,n_x^0\,\left[H_y^\infty(aq) - H_x^\infty(aq)\right]}$$

or,

$$\mathrm{H(aq;\,A=0) = n_1\,H_1^*(\ell) + n_x^0\,H_x^\infty(aq) + \alpha\,n_x^0\,\Delta_r H^\infty(aq)}$$

We assume that $\Delta_\mathrm{r}\mathrm{H^\infty(aq)}$ is independent of temperature together with the amount $\mathrm{n_1}$. Then,

$$\mathrm{C_p(aq;\,A=0)} = \left(\frac{\partial \mathrm{H(aq:\,A=0)}}{\partial \mathrm{T}}\right)_\mathrm{p}$$

Hence,

$$C_p(aq; A = 0) = \left\{n_1 C^*_{p1}(\ell) + n^0_x C^\infty_{px}(aq)\right\} + \Delta_r H^\infty(aq)\, n^0_x(\, d\alpha/dT)$$

The terms in the { } brackets are not (formally) dependent on temperature and constitute a frozen contribution to $C_p(aq, A = 0)$, $C_p(aq : \xi)$. Then equations (d) and (i) yield an equation for $C_p(aq : A = 0)$ in terms of $[\Delta_r H^\infty(aq)]^2$.

$$C_p(aq; A = 0) = C_p(\xi : aq) + \left[\frac{[\Delta_r H^\infty(aq)]^2}{RT^2}\,\frac{K^0}{[1 + K^0]^2}\right] n^0_x$$

in terms of one mole of chemical substance X (i.e. $n^0_x = 1$ mol) [6],

$$C_p(aq; A = 0) = C_p(\xi; aq) + \left[\frac{[\Delta_r H^\infty(aq)]^2}{R\,T^2}\,\frac{K^0}{[1 + K^0]^2}\right]$$

According to equation (k) a large equilibrium heat capacity is favoured by a high $C_p(\xi; aq)$ and a large enthalpy of reaction. The term $[\Delta_r H^\infty(aq)]^2$ ensures that irrespective of whether the reaction (as written) is exothermic or endothermic, $C_p(A = 0) - C_p(\xi)$ is positive. The dependence of $[C_p(aq : A = 0) - C_p(\xi : aq)]$ on temperature forms a bell-shaped plot covering the range of temperatures when all added substance X is completely in the form of X or of Y. The maximum in the bell occurs near the temperature at which K^0 is unity [7]. If K^0 is unity, at this temperature $\Delta_r G^0$ is zero. In other words, at this temperature the reference chemical potentials of X and Y, $\mu^0(X)$ and $\mu^0(Y)$ respectively are equal. Clearly therefore the temperature at the maximum in $C_p(\, A = 0) - C_p(\xi)$ is characteristic of the two solutes [8]. Equation (k) forms the basis of the technique of differential scanning calorimetry (DSC) as applied to the investigation of the thermal stability of biologically important macromolecules [2,9,10]. In the text book case, a plot of isobaric heat capacity against temperature forms a bell-shaped curve, the maximum corresponding to temperature at which the equilibrium constant for an equilibrium having the simple form discussed above is unity. The area under the curve yields the enthalpy change characterising the transition between the two forms X and Y of a single substance.

The possibility exists that the temperature dependences of$\mu^0(X)$ and $\mu^0(Y)$ are such that the two plots intersect at two temperatures producing two maxima in the plot of $C_p(A = 0) - C_p(\xi)$ against temperature.

The patterns recorded by DSC scans for a X $\leftrightarrows$ Y system can be understood in terms of the separate dependences of (μ^0_X/T) and (μ^0_Y/T) on temperature, where $\mu^0(X)$ and $\mu^0(Y)$ are the standard chemical potentials of substances X and Y. The maximum in the recorded heat capacity occurs where the plots of (μ^0_X/T) and (μ^0_Y/T) against temperature cross [11,12]. If these curves have a more complicated shape there is the possibility that they will cross at two temperatures. In fact this observation raises the possibility of identifying hot and cold denaturation of proteins using DSC. Similar extrema in isobaric heat capacities are recorded for gel-to-liquid transitions in vesicles [13,14].

In more complex systems, the overall DSC scan can indicate the presence of domains in a macromolecule which undergo structural changes when the temperature is raised [15,16].

Analysis of extrema in heat capacities becomes somewhat more complicated when two or more equilibria are coupled [17,18].

Footnotes

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[4] From equation (b)

$$\frac{d\alpha}{dT} = \frac{d}{dT}\left[K^0\,(1 + K^0)^{-1}\right] = \left[\frac{1}{1 + K^0} - \frac{K^0}{(1 + K^0)^2}\right]\frac{dK}{dT}$$
$$= \frac{1}{(1 + K^0)^2}\,\frac{dK^0}{dT} = \frac{K^0}{(1 + K^0)^2}\,\frac{1}{K^0}\,\frac{dK^0}{dT} = \frac{K^0}{(1 + K^0)^2}\left[\frac{d\ln K^0}{dT}\right]$$

[5] $\frac{d\alpha}{dT} = \frac{1}{[\,J\,K^{-1}\,mol^{-1}]}\,\frac{1}{[\,K]^2}\,\frac{[1]}{[1]}\,\left[Jmol^{-1}\right] = \frac{1}{[\,K]}$

[6] $\frac{[\Delta_r H^\infty(aq)]^2}{R\,T^2}\,\frac{K^0}{[1+K^0]^2} = \frac{[Jmol^{-1}]^2}{[\,J\,K^{-1}\,mol^{-1}]K]^2}\,\frac{[1]}{[1]^2} = [JK^{-1}\,mol^{-1}]$

[7] With $h = \Delta_r H^\infty(aq)$, the second term in equation (k) can be written as follows $y = \frac{h^2}{R\,T^2}\,\frac{K^0}{(1+K^0)^2}$. The pattern formed by the dependence of y on temperature is given by

$$\frac{dy}{dT} = \frac{h^2}{R\,T^2}\left[\frac{1}{(1+K^0)^2} - \frac{2\,K^0}{(1+K^0)^3}\right]\frac{dK^0}{dT} - \frac{2\,h^2\,K^0}{R\,T^3\,(1+K^0)^2}$$

Or,

$$\frac{dy}{dT} = \frac{h^2\,K^0}{R\,T^2\,(1+K^0)^2}\left[\frac{1-K^0}{(1+K^0)}\,\frac{d\ln(K^0)}{dT} - \frac{2}{T}\right]$$

Since $d\ln(K^0)/dT = h/R\,T^2$, then

$$\frac{dy}{dT} = \frac{h^2\,K^0}{R\,T^3\,(1+K^0)^2}\left[\frac{1-K^0}{(1+K^0)}\,\frac{h}{R\,T} - 2\right]$$

Hence the condition for an extremum in y as a function of T is $\frac{1-K^0}{(1+K^0)}\,\frac{h}{R\,T} - 2 = 0$ Or $\frac{1-K^0}{(1+K^0)} = \frac{2\,R\,T}{h}$ Then

$$K^0 = \frac{1-(2\,R\,T/h)}{1+(2\,R\,T/h)}$$

By definition $h = \Delta_r H^\infty(aq)$. Therefore if the magnitude of $\Delta_r H^\infty(aq)$ is much larger than $2\ R\,T$, the top of the bell shaped curve is reached at a temperature where K^0 is unity. In the general case, at approximately this temperature y is a maximum.

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1.12.7: Expansions- Isobaric and Isentropic

The volume of a closed system at thermodynamic equilibrium containing two chemical substances is defined by equation (a).

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2,\ \mathrm{A} = 0, \xi^{\mathrm{eq}}\right]$$

At temperature T and pressure p, the chemical composition / organisation ξ^{eq} corresponds to the state where the affinity for spontaneous change is zero.

Isobaric Expansions

The system is displaced by a change in temperature to a neighbouring state where the affinity for spontaneous change is also zero; the organisation/composition changes to $\xi^{\mathrm{eq}}(\mathrm{new})$.

$$\mathrm{V}(\ \mathrm{new}\ ) = \mathrm{V}\left[\mathrm{T}(\ \mathrm{new}\ ), \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2,\ \mathrm{A} = 0, \xi^{\mathrm{eq}}(\ \mathrm{new}\ )\right]$$

The differential dependence on temperature of the volume defined in equation. (a) is the equilibrium isobaric thermal expansion, $\mathrm{E}_{\mathrm{p}}(\mathrm{A} = 0)$ [1].

$$\mathrm{E}_{\mathrm{p}}(\mathrm{A} = 0) = \left(\frac{\partial \mathrm{V}}{\partial T}\right)_{\mathrm{p,A}=0}$$

The chemical composition/organisation changes to hold the affinity for spontaneous change at zero. Indeed the perturbation in the form of a change in temperature might have to be extremely slow so that the change in organisation/chemical composition keeps in step with the change in temperature.

The isobaric expansion $\mathrm{E}_{\mathrm{p}}(\mathrm{aq})$ for an aqueous solution containing solute j is related to the partial molar isobaric expansions of solute and solvent; equation (d).

$$\mathrm{E}_{\mathrm{p}}(\mathrm{aq}) = \mathrm{n}_1\, \mathrm{E}_{\mathrm{pl}}(\mathrm{aq}) + \mathrm{n}_{\mathrm{j}}\, \mathrm{E}_{\mathrm{pj}}(\mathrm{aq})$$

Alternatively using the concept of an apparent molar property, we define an (equilibrium) apparent molar isobaric expansion for solute j, $\phi\left(E_{pj}\right)$.

$$\mathrm{E}_{\mathrm{p}}(\mathrm{aq}) = \mathrm{n}_1\, \mathrm{E}^{*}_{\mathrm{pl1}}(\ell) + \mathrm{n}_{\mathrm{j}}\, \phi\left(\mathrm{E}_{\mathrm{pj}}\right)$$

$$\phi\left(\mathrm{E}_{\mathrm{pj}}\right) = \left[\partial \phi\left(\mathrm{V}_{\mathrm{j}}\right) / \partial \mathrm{T}\right]_{\mathrm{p}}$$

Isentropic Expansions

Generally little interest has been shown in either partial molar or apparent molar isentropic expansions of solutes. Complications are encountered in understanding isentropic expansions without the redeeming feature of practical accessibility via an analogue of the Newton -Laplace equation. The isentropic expansions $\mathrm{E}_{\mathrm{S}}(\mathrm{aq})$ is defined by equation (g).

$$\mathrm{E}_{\mathrm{S}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{S(aq)}}$$

The constraint on the partial derivative refers to the entropy of the solution $\mathrm{S}(\mathrm{aq})$. As we change the amount of solute nj for fixed temperature and fixed pressure and amount of solvent n_1, so both $\mathrm{V}(\mathrm{aq})$ and $\mathrm{S}(\mathrm{aq})$ change yielding a new isentropic thermal expansion, $\mathrm{E}_{\mathrm{S}}(\mathrm{aq})$ at a new entropy $\mathrm{S}(\mathrm{aq})$. For a series of solutions having different molalities of solute, comparison of $\mathrm{E}_{\mathrm{S}}(\mathrm{aq})$ is not straightforward because \({\mathrm{S}(\mathrm{aq})\) is itself a function of solution composition. Further comparison cannot be readily drawn with the isentropic thermal expansion of the solvent, $\mathrm{E}^{*}_{\mathrm{SI}}(\ell)$; equation (h).

$$\mathrm{E}^{*}_{\mathrm{S1}}(\ell) = \left(\frac{\partial \mathrm{V}^{*}_{1}(\ell)}{\partial \mathrm{T}}\right) \quad \text{at constant} \quad \mathrm{S}^{*}_{1}(\ell)$$

$\mathrm{E}_{\mathrm{S}}(\mathrm{aq})$ is a non-Gibbsian property. Consequently familiar thermodynamic relationships involving partial molar properties are not valid in the case of partial molar isentropic thermal expansions which are non-Lewisian properties. $\left(\frac{\partial \mathrm{V}_{\mathrm{j}}}{\partial \mathrm{T}}\right)_{\mathrm{s(aq)}}$ is a semi-partial property.

Footnote

[1] For a system at equilibrium where $\mathrm{A} = 0$, $\frac{\partial^2 G}{\partial T\, \partial p} = \frac{\partial^2 G}{\partial p\, \partial T}$

Therefore, $\mathrm{E_p(A = 0)} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p,A=0}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{T,A=0}}$

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1.12.8: Expansions- Solutions- Isobaric- Partial and Apparent Molar

The volume of a given aqueous solution containing n_1 moles of water and n_j moles of solute j is related to the composition by equation (a).

$$\mathrm{V(aq) = n_1\,V_1(aq) + n_j\,V_j(aq)}$$

$\mathrm{V_1(aq)}$ and $\mathrm{V}_j\mathrm{(aq)}$ are the partial molar volumes of water and solute j respectively. The (equilibrium) isobaric thermal expansion of the solution (at fixed pressure) $\mathrm{E_p}$ characterises the differential dependence of $\mathrm{V(aq)}$ on temperature.

$$\mathrm{E_p(aq) = [\partial V(aq)/\partial T]_{p,A=0}}$$

$\mathrm{E_p(aq)}$ is an extensive property of the solution [1]. Two partial molar isobaric thermal expansions are defined, characteristic of solute and solvent [2].

$$\mathrm{E_{p1}(aq) = (\partial V_1(aq)/\partial T)_p}$$

$$\mathrm{E_{pj}(aq) = (\partial V_j(aq)/\partial T)_p}$$

From equation (a),

$$\mathrm{E_p(aq) = n_1\,E_{p1}(aq) + n_j\,E_{pj}(aq)}$$

In the treatment of volumetric properties of solutions we define an apparent molar volume of the solute, $\phi\,(\mathrm{V_j})$. By analogy we rewrite equation (e) in a form which defines the apparent molar isobaric expansion of the solute, $\phi\,(\mathrm{E_j})$. Thus,

$$\mathrm{E_p(aq) = n_1\,E^*_{p1}(\ell) + n_j\,\phi\,(E_{pj})}$$

Here [3],

$$\mathrm{\phi\,(E_{pj}) = \left(\frac{\partial \phi\,(V_j)}{\partial T}\right)_p}$$

For the pure solvent,

$$\mathrm{E^*_{p1}(\ell) = \left(\frac{\partial V^*_1(\ell)}{\partial T}\right)_p}$$

Footnotes

[1] $\mathrm{E_p}$ is an extensive property; the larger the volume V the larger the change in volume for a given increase in temperature.

[2] $E_p = [m^3K^{-1}]$ $\quad E_{p1} = [\mathrm{m^3\ K^{-1}\ mol^{-1}}]$ $\quad E_{pj} = [\mathrm{m^3\ K^{-1}\ mol^{-1}}]$

[3] $\phi\,(\mathrm{E_j}) = [\mathrm{m^3\ K^{-1}\ mol^{-1}}]$

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1.12.9: Expansions- Apparent Molar Isobaric- Composition Dependence

For many aqueous solutions at ambient temperature and pressure the dependence of apparent molar isobaric expansions for solute j $\phi\left(E_{pj}\right)$ on molality m_j is accounted for using an equation having the following general form. [The reason for choosing the molality scale is that m_j is independent of T and p whereas concentration c_j is not.

$$\phi\left(E_{pj}\right) = a_1 + a_2\ \left(m_j/m^0\right) + a_3\ \left(m_j/m^0\right)^2 \ldots\ldots$$

At low solute molalities the linear term is dominant. Granted therefore that equation (a) accounts for the observed pattern, we need to explore the analysis a little further. There are advantages in linking $\phi\left(E_{pj}\right)$ and the partial molar property $\mathrm{E}_{pj}(\mathrm{aq})$.

For an aqueous solution prepared using $1\ \mathrm{kg}$ of water and m_j moles of solute j at fixed T and p,

$$\mathrm{V}\left(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}\right) = \left(1/\mathrm{M}_1\right)\ \mathrm{V}_1^*(\ell) + \mathrm{m_j}\,\phi\left(\mathrm{V_j}\right)$$

Hence,

$$\mathrm{E_p}\left(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}\right) = \left(1/\mathrm{M}_1\right)\ \mathrm{E}_{\mathrm{p}1}^*(\ell) + \mathrm{m_j}\,\phi\left(\mathrm{E_{pj}}\right)$$

$$\left(\frac{\partial \mathrm{E_p}\left(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}\right)}{\partial \mathrm{m_j}}\right) = \mathrm{m_j}\ \left(\frac{\partial \phi\left(\mathrm{E_{pj}}\right)}{\partial \mathrm{m_j}}\right) + \phi\left(\mathrm{E_{pj}}\right)$$

But

$$\left(\frac{\partial \mathrm{E_p}\left(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}\right.}{\partial \mathrm{m_j}}\right) = \mathrm{E_{pj}}(\mathrm{aq})$$

$$\mathrm{E_{pj}}(\mathrm{aq}) = \mathrm{m_j}\ \left(\frac{\partial \phi\left(\mathrm{E_{pj}}\right)}{\partial \mathrm{m_j}}\right) + \phi\left(\mathrm{E_{pj}}\right)$$

Hence the partial molar isobaric expansions for solute j can be calculated using the apparent molar isobaric expansions and its dependence on molality. Further if equation (a) accounts for the dependence of $\phi\left(\mathrm{E_{pj}}\right)$ on m_j, then

$$\mathrm{E_{pj}} = \mathrm{a}_1 + 2\,\mathrm{a}_2\ \left(\mathrm{m_j}/\mathrm{m}^0\right) + 3\,\mathrm{a}_3\ \left(\mathrm{m_j}/\mathrm{m}^0\right)^2 \ldots\ldots$$

Therefore, using equations (a) and (g),

$$\mathrm{limit}\ \left(\mathrm{m_j} \to 0\right)\phi\left(\mathrm{E_{pj}}\right) = \phi\left(\mathrm{E_{pj}}\right)^\infty = \mathrm{E_{pj}^\infty}(\mathrm{aq})$$

In the next stage of the analysis we develop an argument starting with an equation for the chemical potential of solute j in solution.

$$\mu_j(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right) + \int_{\mathrm{p}^0}^{p}\ \mathrm{V_j^\infty}(\mathrm{aq};\mathrm{T})\,\mathrm{dp}$$

Then with $\mathrm{V_j}(\mathrm{aq}) = \left(\frac{\partial \mu_\mathrm{j}(\mathrm{aq})}{\partial \mathrm{p}}\right)_\mathrm{T}$,

$$\mathrm{V_j}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{V_j^\infty}(\mathrm{aq}) + \mathrm{R\,T}\ \left[\partial \ln\left(\gamma_\mathrm{j}\right)/\partial \mathrm{p}\right]_\mathrm{T}$$

With $\mathrm{E_{pj}}(\mathrm{aq}) = \left(\frac{\partial \mathrm{V_j}(\mathrm{aq})}{\partial \mathrm{T}}\right)_\mathrm{p}$,

$$\mathrm{E_{pj}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{E_{pj}^\infty}(\mathrm{aq}) + \mathrm{R}\ \left(\frac{\partial \ln\left(\gamma_\mathrm{j}\right)}{\partial \mathrm{p}}\right)_\mathrm{T} + \mathrm{R\,T}\ \left(\frac{\partial^2 \ln\left(\gamma_\mathrm{j}\right)}{\partial \mathrm{p}\,\partial \mathrm{T}}\right)$$

In the case of dilute solutions we might assert that $\ln\left(\gamma_\mathrm{j}\right)$ is a linear function of molality m_j. Thus[1],

$$\ln\left(\gamma_\mathrm{j}\right) = \mathrm{S}_\gamma\ \left(\mathrm{m_j}/\mathrm{m}^0\right)$$

By definition [2], $\mathrm{S_V} = \left(\frac{\partial \mathrm{S}_\gamma}{\partial \mathrm{p}}\right)_\mathrm{T}$ and[3] $\mathrm{S_{Ep}} = \mathrm{S_V} + \mathrm{T}\ \left(\frac{\partial \mathrm{S_V}}{\partial \mathrm{T}}\right)_\mathrm{p}$ Then[4]

$$\mathrm{E_{pj}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{E_{pj}^\infty}(\mathrm{aq}) + \mathrm{R\,S_{Ep}}\ \left(\mathrm{m_j}/\mathrm{m}^0\right)$$

Thus we identify the basis of the parameter a2 in equation (a).

Footnotes

[1] $\ln(\gamma_j) = [1]\ [\mathrm{molkg^{-1}}]\ [\mathrm{molkg^{-1}}]^{-1}$

[2] $S_V = [1]/[\mathrm{Nm^{-2}}] = [\mathrm{Nm^{-2}}]^{-1}$

[3] $S_{Ep} = [\mathrm{Nm^{-2}}]^{-1} + [\mathrm{K}]\ [\mathrm{Nm^{-2}}]^{-1}\ [\mathrm{K^{-1}} = [\mathrm{Nm^{-2}}]^{-1}$

[4]

$$\begin{aligned} E_{pj}(aq) &= E_{pj}^{\infty}(aq) + [\mathrm{JK^{-1}\ mol^{-1}}]\ [\mathrm{Nm^{-2}}]^{-1}\ [\mathrm{molkg^{-1}}]\ [\mathrm{molkg^{-1}}]^{-1} \\ &= E_{pj}^{\infty}(aq) + [\mathrm{NmK^{-1}\ mol^{-1}}]\ [\mathrm{Nm^{-2}}]^{-1} \\ &= E_{pj}^{\infty}(aq) + [\mathrm{m^3\ K^{-1}\ mol^{-1}}] \end{aligned}$$

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1.12.10: Expansions- Solutions Apparent Molar Isobaric Expansions- Determination

The volume of an aqueous solution $\mathrm{V(aq)}$ is related to the amounts of solvent and solute through the molar volume of water $\mathrm{V_1^*(\ell)}$ and the apparent molar volume of solute \(\phi \left(\mathrm{V}_{j}\right) at the same temperature and pressure; equation (a).

$$\mathrm{V(aq) = n_1\, V_1^*(\ell) + n_j\, \phi\,(V_j)}$$

The isobaric temperature dependence of the apparent molar volume of solute $\phi\,(\mathrm{V_j})$ yields the apparent molar (isobaric) expansion of solute j, $\phi\,(\mathrm{E}_j)$.

$$\phi\,(E_{pj}) = \left(\frac{\partial \phi\,(V_j)}{\partial T}\right)_p$$

Equation (a) (as in most treatments of volumetric properties) is the starting equation for the development of equations which relate apparent molar isobaric expansions of a solute j to the measured isobaric expansibilities of solvent and solution. The following four equivalent equations are frequently quoted [1-8]. A method is also available for direct determination of $\mathrm{E_{pj}(aq)}$ from density data determined as functions of T and m_j [9].

Molality Scale [1-3]

$$\mathrm{\phi\,(E_{pj}) = [m_j\, \rho_1^*(\ell)]^{-1}\ \left[\alpha_p(aq) - \alpha_{pl}^*(\ell)\right] + \alpha_p(aq)\, \phi\,(V_j)}$$

$$\phi\,(E_{pj}) = [m_j\, \rho(aq)\, \rho_1^*(\ell)]^{-1}\ \left[\alpha_p(aq)\, \rho_1^*(\ell) - \alpha_{p1}^*(\ell)\, \rho(aq)\right] + \alpha_p(aq)\, M_j\, [\rho(aq)]^{-1}$$

Concentration Scale [4 - 7]

$$\mathrm{\phi\,(E_{pj}) = \left[\frac{1}{c_j\, \rho_1^*(\ell)}\right]\ \left[\alpha_p(aq)\, \rho_1^*(\ell) - \rho(aq)\, \alpha_{pl}^*(\ell)\right] + \alpha_{p1}^*(\ell)\, M_j/\rho_1^*(\ell)}$$

$$\mathrm{\phi\,(E_{pj}) = [c_j]^{-1}\ \left[\alpha_p(aq) - \alpha_{pl}^*(\ell)\right] + \phi\,(V_j)\ \alpha_{p1}^*(\ell)}$$

The four equations (c) - (f) are thermodynamically correct, no assumptions being made in their derivation.

The partial molar isobaric expansion $\mathrm{E_{pj}(aq)}$ is obtained using equation (g) [8].

$$E_{pj}(aq) = \phi\,(E_{pj}) + m_j \left(\frac{\partial \phi\,(E_{pj})}{\partial m_j}\right)_p$$

Footnotes

[1] From equation (a) with respect to the dependence of $\mathrm{V(aq}$ on temperature at constant p and at "$\mathrm{A = 0}$".

$$\mathrm{(\partial V(aq)/\partial T)_p = n_1\ (\partial V_1^*(\ell)/\partial T)_p + n_j\ (\partial \phi\,(V_j)\,/\partial T)_p}$$

Using equation (b), $\mathrm{(\partial V(aq)/\partial T)_p = n_1\ (\partial V_1^*(\ell)/\partial T)_p + n_j\, \phi\,(E_{pj})}$ Hence,

$$\left(\frac{1}{V(aq)}\right)\left(\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right)_p = \mathrm{n_1}\left(\frac{\mathrm{V_1^*(\ell)}}{\mathrm{V_1^*(\ell)}}\right)\frac{1}{\mathrm{V(aq)}}\left(\frac{\partial \mathrm{V_1^*(\ell)}}{\partial \mathrm{T}}\right)_p + \left(\frac{\mathrm{n_j}}{\mathrm{V(aq)}}\right)\phi\,(\mathrm{E_{pj}})$$

Thus, $\mathrm{\alpha_p(aq) = n_1\left(\frac{V_1^*(\ell)}{V(aq)}\right)\ \alpha_{p1}^*(\ell) + \frac{n_j}{V(aq)}\,\phi\,(E_{pj})}$ or, $\mathrm{V(aq)\,\alpha_p(aq) = n_1\, V_1^*(\ell)\,\alpha_{p1}^*(\ell) + n_j\,\phi\,(E_{pj})}$

We again use equation (a) for $\mathrm{V(aq}$,

$$\mathrm{n_j\, \phi\,(E_{pj}) = [n_1\, V_1^*(\ell) + n_j\, \phi\,(V_j)]\ \alpha_p(aq) - n_1\, V_1^*(\ell)\, \alpha_{pl}^*(\ell)}$$

But, $\mathrm{V_1^*(\ell) = M_1/\rho_1^*(\ell)}$ where $\mathrm{M_1}$ is the molar mass of the solvent water.

$$\phi\,(E_{pj}) = \frac{n_1\, M_1}{n_j\, \rho_1^*(\ell)}\,\alpha_p(aq) - \frac{n_1\, M_1}{n_j\, \rho_1^*(\ell)}\,\alpha_1^*(\ell) + \alpha_p(aq)\,\phi\,(V_j)$$

But $\mathrm{m_j = n_j/n_l\, M_l}$.

$$\phi\left(\mathrm{E_{pj}}\right)=\left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\,\left[\alpha_\mathrm{p}(\mathrm{aq})-\alpha_{\mathrm{p1}}^*(\ell)\right]+\alpha_\mathrm{p}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$

Hence we obtain equation (c).

[2] With reference to equation (c),

$$\left[\frac{1}{\mathrm{m_j}\,\rho_1^*(\ell)}\right]\,\left[\alpha_\mathrm{p}(\mathrm{aq})-\alpha_{\mathrm{p1}}^*(\ell)\right]=\left[\frac{\mathrm{kg}}{\mathrm{mol}}\right]\,\left[\frac{\mathrm{m^3}}{\mathrm{kg}}\right]\,\left[\mathrm{K^{-1}}\right]=\left[\mathrm{m^3\ K^{-1}\ mol^{-1}}\right]$$
$$\alpha_\mathrm{p}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)=\left[\mathrm{K^{-1}}\right]\,\left[\mathrm{m^3\ mol^{-1}}\right]$$

[3] From $\phi\left(\mathrm{E_{pj}}\right)=\left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\,\left[\alpha_\mathrm{p}(\mathrm{aq})-\alpha_{\mathrm{p1}}^*(\ell)\right]+\alpha_\mathrm{p}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$ and, $\phi\left(\mathrm{V_j}\right)=\frac{\mathrm{V(aq)-n_1\,V_1^*(\ell)}}{\mathrm{n_j}}$

$$\phi\left(E_{pj}\right)=\left[m_j\,\rho_1^*(\ell)\right]^{-1}\,\left[\alpha_p(aq)-\alpha_{pl}^*(\ell)\right]+\alpha_p(aq)\,\left[\frac{\mathrm{V(aq)-n_1\,V_1^*(\ell)}}{\mathrm{n_j}}\right]$$

$$\phi\left(E_{pj}\right)=\left[m_j\,\rho_1^*(\ell)\right]^{-1}\,\left[\alpha_p(\mathrm{aq})-\alpha_{p1}^*(\ell)\right]+\alpha_p(\mathrm{aq})\,\left[\frac{1}{\mathrm{c}_j}-\frac{\mathrm{n_1\,M_1}}{\rho_1^*(\ell)\,\mathrm{n_j}}\right]$$

But $\frac{1}{c_j}=\frac{M_j}{\rho(aq)}+\frac{1}{m_j\,\rho(aq)}$

$$\phi\left(E_{\mathrm{pj}}\right)=\left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\,\left[\alpha_\mathrm{p}(\mathrm{aq})-\alpha_{\mathrm{pl}}^*(\ell)\right]+\left[\frac{\alpha_\mathrm{p}(\mathrm{aq})}{\mathrm{m_j}\,\rho(\mathrm{aq})}+\frac{\alpha_\mathrm{p}(\mathrm{aq})\,\mathrm{M_j}}{\rho(\mathrm{aq})}-\frac{\alpha_\mathrm{p}(\mathrm{aq})}{\rho_1^*(\ell)\,\mathrm{m_j}}\right]$$
$$\phi\left(\mathrm{E_{pj}}\right)=\frac{\alpha_\mathrm{p}(\mathrm{aq})}{\mathrm{m_j}\,\rho_1^*(\ell)}-\frac{\alpha_{\mathrm{pl}}^*(\ell)}{\mathrm{m_j}\,\rho_1^*(\ell)}+\frac{\alpha_\mathrm{p}(\mathrm{aq})}{\mathrm{m_j}\,\rho(\mathrm{aq})}+\frac{\alpha_\mathrm{p}(\mathrm{aq})\,\mathrm{M_j}}{\rho(\mathrm{aq})}-\frac{\alpha_\mathrm{p}(\mathrm{aq})}{\rho_1^*(\ell)\,\mathrm{m_j}}$$

Hence we obtain equation (d).

$$\phi\left(E_{pj}\right)=\left[m_j\,\rho(aq)\,\rho_1^*(\ell)\right]^{-1}\,\left[\alpha_p(aq)\,\rho_1^*(\ell)-\alpha_{p1}^*(\ell)\,\rho(aq)\right]$$
$$+\alpha_p(aq)\,M_j\left[\rho(aq)\right]^{-1}$$

[4] From $\left(\partial\mathrm{V(aq)}/\partial\mathrm{T}\right)_\mathrm{p}=\mathrm{n_1}\,\left(\partial\mathrm{V_1^*}(\ell)/\partial\mathrm{T}\right)_\mathrm{p}+\mathrm{n_j}\,\phi\left(\mathrm{E_{pij}}\right)$

$$\alpha_\mathrm{p}(\mathrm{aq})\,\mathrm{V(aq)}=\mathrm{n_1\,V_1^*}(\ell)\,\alpha_{\mathrm{p1}}^*(\ell)+\mathrm{n_j}\,\phi\left(\mathrm{E_{pjj}}\right)$$

Or, $\mathrm{n_j}\,\phi\left(\mathrm{E_{pj}}\right)=\mathrm{V(aq)}\,\alpha_\mathrm{p}(\mathrm{aq})-\mathrm{n_1\,V_1^*}(\ell)\,\alpha_{\mathrm{p1}}^*(\ell)$

But, $\rho(\mathrm{aq})=\left(\mathrm{n_1\,M_1}+\mathrm{n_j\,M_j}\right)/\mathrm{V(aq)}$ or, $\mathrm{n_1}=\left(\mathrm{V(aq)}\,\rho(\mathrm{aq})-\mathrm{n_j\,M_j}\right)/\mathrm{M_1}$

$$n_j\,\phi\left(E_{pj}\right)=\left[V(aq)\,\alpha_p(aq)\right]-\left[V(aq)\,\rho(aq)-n_j\,M_j\right]\,V_1^*(\ell)\,\alpha_{pl}^*(\ell)/M_1$$
$$\phi\left(E_{pj}\right)=\left[\frac{V(aq)\,\alpha_p(aq)}{n_j}\right]-\left[\frac{V(aq)\,\rho(aq)\,V_1^*(\ell)\,\alpha_1^*(\ell)}{n_j\,M_1}\right]+\left[\frac{V_1^*(\ell)\,\alpha_{p1}^*(\ell)\,M_j}{M_1}\right]$$

But concentration $\mathrm{c_j}=\mathrm{n_j}/\mathrm{V(aq)}$ and $\rho_1^*=\mathrm{M_1}/\mathrm{V_1^*}(\ell)$.

$$\phi\left(\mathrm{E_j}\right)=\left[\frac{\alpha_\mathrm{p}(\mathrm{aq})}{\mathrm{c_j}}\right]-\left[\frac{\rho(\mathrm{aq})\,\alpha_{\mathrm{pl}}^*(\ell)}{\mathrm{c_j}\,\rho_1^*(\ell)}\right]+\left[\frac{\alpha_{\mathrm{p1}}^*(\ell)\,\mathrm{M_j}}{\rho_1^*(\ell)}\right]$$

Hence we obtain equation (e).

$$\phi\left(E_{pj}\right)=\left[\frac{1}{c_j\,\rho_1^*(\ell)}\right]\,\left[\alpha_p(\mathrm{aq})\,\rho_1^*(\ell)-\rho(aq)\,\alpha_{p1}^*(\ell)\right]+\alpha_{p1}^*(\ell)\,M_j/\rho_1^*(\ell)$$

[5] With reference to equation (e),

$$\left[\frac{1}{\mathrm{c_j}\,\rho_1^*(\ell)}\right]\,\left[\alpha_\mathrm{p}(\mathrm{aq})\,\rho_1^*(\ell)-\rho(\mathrm{aq})\,\alpha_{\mathrm{pl1}}^*(\ell)\right]=\left[\frac{\mathrm{m^3}}{\mathrm{mol}}\right]\,\left[\frac{\mathrm{m^3}}{\mathrm{kg}}\right]\,\left[\mathrm{K^{-1}}\right]\,\left[\mathrm{kgm^{-3}}\right]$$
$$=\left[\mathrm{m^3\ K^{-1}\ mol^{-1}}\right]$$

[6] The volume of a solution, $\mathrm{V(aq)}=\mathrm{n_1\,V_1^*}(\ell)+\mathrm{n_1}\,\phi\left(\mathrm{V_j}\right)$

Concentration $\mathrm{c_j}=\mathrm{n_j}/\mathrm{V(aq)}$ or, $\mathrm{c_j}=\frac{\mathrm{n_j}}{\mathrm{n_1\,V_1^*}(\ell)+\mathrm{n_j}\,\phi(\mathrm{V_j})}$

But molality $\mathrm{m_j}=\mathrm{n_j}/\mathrm{n_l\,M_l}$ $\mathrm{c_j}=\frac{\mathrm{m_j\,n_1\,M_1}}{\mathrm{n_1\,V_1^*}(\ell)+\mathrm{n_j}\,\phi(\mathrm{V_j})}$ or, $\frac{1}{\mathrm{c_j}}=\frac{\mathrm{n_1\,V_1^*}(\ell)}{\mathrm{m_j\,n_1\,M_1}}+\frac{\mathrm{n_j}\,\phi(\mathrm{V_j})}{\mathrm{n_1\,M_1\,m_j}}$ or, $\frac{1}{c_j}=\frac{1}{m_j\,\rho_1^*(\ell)}+\phi\left(V_j\right)$ or, $\frac{1}{\mathrm{m_j}}=\frac{\rho_1^*(\ell)}{\mathrm{c_j}}-\rho_1^*(\ell)\,\phi\left(\mathrm{V_j}\right)$

From equation (c).

$$\phi\left(\mathrm{E_{pj}}\right)=\left[\frac{1}{\rho_1^*(\ell)}\right]\left[\frac{\rho_1^*(\ell)}{\mathrm{c_j}}-\rho_1^*(\ell)\,\phi\left(\mathrm{V_j}\right)\right]\left[\alpha_{\mathrm{p}}(\mathrm{aq})-\alpha_{\mathrm{p1}}^*(\ell)\right]+\alpha_{\mathrm{p}}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$

Or,

$$\phi\left(\mathrm{E_{pj}}\right)=\left[\frac{1}{\mathrm{c_j}}\right]\left[\alpha_{\mathrm{p}}(\mathrm{aq})-\alpha_{\mathrm{pl}}^*(\ell)\right]-\phi\left(\mathrm{V_j}\right)\,\alpha_{\mathrm{p}}(\mathrm{aq})+\phi\left(\mathrm{V_j}\right)\,\alpha_{\mathrm{pl}}^*(\ell)+\alpha_{\mathrm{p}}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$

We obtain equation (f)

$$\phi\left(\mathrm{E_{pj}}\right)=\left[\mathrm{c_j}\right]^{-1}\left[\alpha_{\mathrm{p}}(\mathrm{aq})-\alpha_{\mathrm{pl}}^*(\ell)\right]+\phi\left(\mathrm{V_j}\right)\,\alpha_{\mathrm{pl}}^*(\ell)$$

[7] With reference to equation (f)

$$\left[\frac{1}{\mathrm{c_j}}\right]\left[\alpha_{\mathrm{p}}(\mathrm{aq})-\alpha_{\mathrm{pl}}^*(\ell)\right]=\left[\frac{\mathrm{m}^3}{\mathrm{mol}}\right]\left[\mathrm{K}^{-1}\right]=\left[\mathrm{m}^3\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}\right]$$

[8] From $\mathrm{E_p(aq)=n_1\,E_{p1}^*(\ell)+n_j\,\phi\left(E_{pj}\right)}$ Then, $\left(\frac{\partial E_p}{\partial n_j}\right)_{T,p,n_j}=n_j\left[\frac{\partial\phi(E_{pj})}{\partial n_j}\right]+\phi\left(E_{pj}\right)$

Or, $\mathrm{E_{pj}(aq)=m_j\left[\frac{\partial\phi(E_{pj})}{\partial m_j}\right]+\phi\left(E_{pj}\right)}$

[9] M. J. Blandamer and H. Hoiland, Phys.Chem.Chem.Phys.,1999,**1**,1873.

This method starts out with the measured dependence of the density $\rho(\mathrm{aq})$ on temperature and molality at fixed pressure about density $\rho_1^*(\ell,\theta)$, at temperature θ at same pressure. For example the data might be fitted to an equation having the following form yielding the b-coefficients.

$$\rho\left(\mathrm{m_j,T}\right)=\rho_1^*(\ell,\theta)+\mathrm{b_2\left(T-\theta\right)\left(m_j/m^0\right)/\theta+b_3\left(T-\theta\right)\left(m_j/m^0\right)^2/\theta}+\mathrm{b_4\left(T-\theta\right)^2\left(m_j/m^0\right)/\theta^2+b_5\left(T-\theta\right)^2\left(m_j/m^0\right)^2/\theta^2}$$

$$\left(\frac{\partial\rho\left(\mathrm{aq;m_j;T}\right)}{\partial\mathrm{T}}\right)_{\mathrm{m_j}}=\mathrm{b_2\left(m_j/m^0\right)/\theta+b_3\left(m_j/m^0\right)^2/\theta+2\,b_4\left(T-\theta\right)\left(m_j/m^0\right)/\theta^2+2\,b_5\left(T-\theta\right)\left(m_j/m^0\right)/\theta^2}$$

and,

$$\left(\frac{\partial\rho\left(\mathrm{aq;m_j;T}\right)}{\partial\left(\mathrm{m_j/m^0}\right)}\right)_{\mathrm{T}}=\mathrm{b_2\left(T-\theta\right)/\theta+2\,b_3\left(T-\theta\right)\left(m_j/m^0\right)/\theta+b_4\left(T-\theta\right)^2/\theta^2+2\,b_5\left(T-\theta\right)^2\left(m_j/m^0\right)/\theta^2}$$

The density $\rho(\mathrm{aq})$ of an aqueous solution molality $\mathrm{m_j}$ prepared using $1\ \mathrm{kg}$ of water is given by the following equation.

$$\rho(\mathrm{aq})=\left[1+\mathrm{M_j\,m_j}\right]/\mathrm{V\left(aq;w_1=1\ kg\right)}$$

$$\mathrm{V\left(aq;w_1=1\ kg\right)}=\left[1+\mathrm{M_j\,m_j}\right]/\rho(\mathrm{aq})$$

Also,

$$\mathrm{V\left(aq;w_1=1\ kg\right)}=(1/\mathrm{M_1})\ \mathrm{V_1(aq)+m_j\,V_j(aq)}$$

$$\left(\frac{\partial\mathrm{V\left(aq;w_1=1\ kg\right)}}{\partial\mathrm{m_j}}\right)_{\mathrm{T,p}}=\frac{\mathrm{M_j}}{\rho(\mathrm{aq})}-\frac{1+\mathrm{M_j\,m_j}}{[\rho(\mathrm{aq})]^2}\left(\frac{\partial\rho(\mathrm{aq})}{\partial\mathrm{m_j}}\right)_{\mathrm{T,p}}$$

But,

$$\mathrm{V_j(aq)}=\left(\frac{\partial\mathrm{V\left(aq;w_1=1\ kg\right)}}{\partial\mathrm{m_j}}\right)_{\mathrm{T,p}}$$

And,

$$E_{pj}(aq) = \left(\frac{\partial V_j(aq)}{\partial T}\right)_{p,m_j}$$

$$\mathrm{E_{pj}(aq)} = \frac{\partial}{\partial \mathrm{T}}\left\{\frac{\mathrm{M_j}}{\rho(\mathrm{aq})} - \left(\frac{1}{\rho(\mathrm{aq})}\right)^2\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{m_j}}\right)[1+\mathrm{M_j\,m_j}]\right\}$$

$$\mathrm{E_{pj}(aq)} = -\frac{\mathrm{M_j}}{(\rho(\mathrm{aq}))^2}\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{T}}\right)_{\mathrm{m_j}} + \frac{2}{(\rho(\mathrm{aq})^3)}\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{T}}\right)_{\mathrm{m_j}}\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{m_j}}\right)[1+\mathrm{M_j\,m_j}]$$
$$-\frac{1}{(\rho(\mathrm{aq}))^2}\frac{\partial}{\partial \mathrm{T}}\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{m_j}}\right)[1+\mathrm{M_j\,m_j}]$$

Using equation (k) in conjunction with equations (a) - (c), partial molar isobaric expansion $\mathrm{E_{pj}(aq)}$ is calculated from the density and its dependence on both temperature and molality of solute. In another development $\mathrm{E_{pj}}$ is related to α_p and its dependence on molality of solute. By definition,

$$\alpha_p(\mathrm{aq}) = -\frac{1}{V(\mathrm{aq})}\left(\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right)_{\mathrm{p,m(j)}}$$

Or,

$$\alpha_p(aq) = -\frac{1}{\rho(aq)}\left(\frac{\partial \rho(aq)}{\partial T}\right)_{p,m(j)}$$

At temperature T and molality m_j,

$$\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{T}}\right)_{\mathrm{p,m(j)}} = -\alpha_\mathrm{p}(\mathrm{aq})\,\rho(\mathrm{aq})$$

Using equation (n)

$$E_{pj}(aq) = \frac{M_j\,\alpha_p}{\rho(aq)} - \frac{2}{(\rho(aq))^2}\alpha_p\left(\frac{\partial \rho(aq)}{\partial m_j}\right)[1+M_j\,m_j]$$
$$-\frac{1}{(\rho(aq))^2}\frac{\partial}{\partial m_j}\left(\frac{\partial \rho}{\partial T}\right)[1+M_j\,m_j]$$

But from equation (n)

$$\frac{\partial}{\partial m_j}\left(\frac{\partial \rho}{\partial T}\right) = -\alpha_p\frac{\partial \rho(\mathrm{aq})}{\partial m_j} - \rho(\mathrm{aq})\left(\frac{\partial \alpha_p}{\partial m_j}\right)$$

Therefore,

$$\mathrm{E_{pj}} = \frac{\mathrm{M_j}\,\alpha_\mathrm{p}}{\rho(\mathrm{aq})} - \frac{2}{(\rho(\mathrm{aq}))^2}\alpha_\mathrm{p}\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{m_j}}\right)[1+\mathrm{M_j\,m_j}]$$
$$+\frac{1}{(\rho(\mathrm{aq}))^2}\alpha_\mathrm{p}\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{m_j}}\right)[1+\mathrm{M_j\,m_j}] + \frac{1}{\rho(\mathrm{aq})}\left(\frac{\partial \alpha_\mathrm{p}}{\partial \mathrm{m_j}}\right)[1+\mathrm{M_j\,m_j}]$$

or, (with reordering of terms)

$$\mathrm{E_{pj}} = -\frac{[1+\mathrm{M_j\,m_j}]}{(\rho(\mathrm{aq}))^2}\alpha_\mathrm{p}\left(\frac{\partial \rho(\mathrm{aq})}{\partial \mathrm{m_j}}\right) + \frac{1+\mathrm{M_j\,m_j}}{\rho(\mathrm{aq})}\left(\frac{\partial \alpha_\mathrm{p}}{\partial \mathrm{m_j}}\right) + \frac{\mathrm{M_j}\,\alpha_\mathrm{p}}{\rho(\mathrm{aq})}$$

Using equation (g) for $\mathrm{V_j(aq)}$

$$\mathrm{E_{pj}} = \mathrm{V_j(aq)}\,\alpha_\mathrm{p} + \frac{[1+\mathrm{M_j\,m_j}]}{\rho(\mathrm{aq})}\left(\frac{\partial \alpha_\mathrm{p}}{\partial \mathrm{m_j}}\right)$$

The partial molar isobaric expansion $\mathrm{E_{pj}}$ is calculated from isobaric expansibility and its dependence on molality of solute.

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1.12.11: Expansions- Isobaric- Apparent Molar- Neutral Solutes

For many aqueous solutions at ambient pressure and temperature, the dependence of $\phi\left(\mathrm{E_{pj}}\right)$ on molality of a neutral solute j, m_j is accounted for by an equation having the following general form. [The reason for choosing the molality scale is again the fact that m_j is independent of T and p but concentration c_j is not.]

$$\phi\left(E_{pj}\right) = a_1 + a_2\ \left(m_j/m^0\right) + a_3\ \left(m_j/m^0\right)^2 + a_4\ \left(m_j/m^0\right)^3 + ...$$

At low molalities, the linear term is dominant. Granted therefore that equation(a) accounts for the observed pattern, we need a quantitative description which accounts for this pattern. There are advantages in linking directly the apparent property $\phi\left(\mathrm{E_{pj}}\right)$ and the partial molar property $\mathrm{E_{pj}(aq)}$.

For an aqueous solution at fixed temperature and pressure,

$$\mathrm{E_{pj}(aq)} = \mathrm{m_j}\left(\frac{\partial\phi\left(\mathrm{E_{pj}}\right)}{\partial \mathrm{m_j}}\right) + \phi\left(\mathrm{E_{pj}}\right)$$

Hence the partial molar isobaric expansion of solute j can be calculated from the apparent molar isobaric expansion and its dependence on molality, m_j. Hence if equation (a) satisfactorily describes the observed dependence of $\phi\left(E_{pj}\right)$ on m_j,

$$\mathrm{E_{pj}(aq)} = \mathrm{a_1} + 2\,\mathrm{a_2}\ \left(\mathrm{m_j/m^0}\right) + 3\,\mathrm{a_3}\ \left(\mathrm{m_j/m^0}\right)^2 + ...$$

Therefore,

$$\mathrm{limit}\left(\mathrm{m_j} \to 0\right)\mathrm{E_{pj}(aq)} = \mathrm{limit}\left(\mathrm{m_j} \to 0\right)\phi\mathrm{E_{pj}(aq)} = \mathrm{E_{pj}^{\infty}(aq)} = \phi\left(\mathrm{E_{pj}}\right)^{\infty}$$

Consequently the parameter $\mathrm{a_1}$ in equations (a) and (b) is the limiting partial molar isobaric expansion of solute j. For dilute solutions, equation (c) takes the following simple form.

$$\mathrm{E_{pj}(aq)} = \mathrm{E_{pj}^{\infty}(aq)} + \mathrm{R\,S_{Ep}}\ \left(\mathrm{m_j/m^0}\right)$$

In these terms we can identify the basis of the parameter $\mathrm{a_2}$ in equations (a) and (c). Desrosiers et al [1] used a quadratic (cf. equation (a)) to express the dependence of $\phi\left(\mathrm{E_{pj}}\right)$ at 298 K on molality of urea in aqueous solutions; $\phi\left(\mathrm{E_{pj}}\right) = 0.07\ \mathrm{cm^3\ K^{-1}\ mol^{-1}}$, coefficient $\mathrm{a_2}$ being positive and coefficient $\mathrm{a_3}$ being negative.

The majority of published information concerns the dependence on temperature of $\phi\left(\mathrm{V_j}\right)^{\infty}$. A survey [2] based on a dilatometric study of 15 non-electrolytes in aqueous solution indicates that $\left[\mathrm{d}\phi\left(\mathrm{V_j}\right)^{\infty}/\mathrm{dT}\right]$ is less than $\left[\mathrm{dV_j^*}(\ell)/\mathrm{dT}\right]$ for the pure liquid substance j; the second derivative $\left[\mathrm{d^2}\phi\left(\mathrm{V_j}\right)^{\infty}/\mathrm{dT^2}\right]$ is positive. However for hydrophilic solutes $\left[\mathrm{d}\phi\left(\mathrm{V_j}\right)^{\infty}/\mathrm{dT}\right]$ is larger than $\left[\mathrm{dV_j^*}(\ell)/\mathrm{dT}\right]$ and $\left[\mathrm{d^2}\phi\left(\mathrm{V_j}\right)^{\infty}/\mathrm{dT^2}\right]$ is negative [3]. A similar pattern is observed for sucrose and urea for which $\left[\mathrm{d^2}\phi\left(\mathrm{V_j}\right)^{\infty}/\mathrm{dT^2}\right]$ is negative. Indeed Hepler [4] classified solutes in aqueous solutions as either structure-breaking (negative) or structure forming (positive) on the basis of the sign for $\left[\mathrm{d^2}\phi\left(\mathrm{V_j}\right)^{\infty}/\mathrm{dT^2}\right]$. The dependence of $\phi\left(V_j\right)^{\infty}$ on temperature for both glycine and alanine in $\mathrm{NaCl(aq)}$ is small [5], For monosacchrides(aq) $\mathrm{E_{pj}^{\infty}(aq)}$ is positive.

Footnotes

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1.12.12: Expansions- Isobaric- Salt Solutions- Apparent Molar

In general terms the dependence of apparent molar isobaric expansions for salt j on the composition of a given solution can be described using the following empirical equation.

$$\phi\left(E_{pj}\right)=a_1+a_2\,\left(m_j/m^0\right)^{1/2}+a_3\,\left(m_j/m^0\right)$$

The presence of a term in $\left(\mathrm{m_j/m^0}\right)^{1/2}$ is not unexpected in the case of salt solutions. Moreover for dilute solutions the term in $\left(\mathrm{m_j/m^0}\right)^{1/2}$ is dominant. Hence

$$\left[\partial\phi\left(E_{pj}\right)/\partial m_j\right]=(1/2)\,a_2\,\left(m_j\,m^0\right)^{-1/2}+a_3\,\left(1/m^0\right)$$

Then,

$$\mathrm{E_{pj}(aq)=a_1+(3/2)\,a_2\,\left(m_j/m^0\right)^{1/2}+2\,a_3\,\left(m_j/m^0\right)}$$

Therefore parameter $\mathrm{a_1}$ is the limiting partial molar and apparent molar isobaric expansion of solute j in solution. An explanation of the term in $\left(m_j/m^0\right)^{1/2}$ based on the Debye-Huckel Limiting Law (DHLL).

In general terms the chemical potential of salt j in aqueous solution at fixed T and p is related to molality $\mathrm{m_j}$ using equation (d).

$$\mu_j(aq)=\mu_j^0(aq)+v\,R\,T\,\ln\left(Q\,m_j\,\gamma_\pm/m^0\right)+\int_{p^0}^{p}V_j^\infty(aq)\,dp$$

$$\mathrm{V_j(aq)=V_j^\infty(aq)+v\,R\,T\,\left(\partial\ln\gamma_\pm/\partial p\right)_T}$$

Therefore

$$\mathrm{E_{pj}(aq)=E_{pj}^\infty(aq)+v\,R\,\left\{\left[d\ln\left(\gamma_\pm\right)/dp\right)\right]_T+T\,\left[d^2\ln\left(\gamma_\pm\right)/dp\,dT\right]\right\}}$$

According to the DHLL,

$$\ln\left(\gamma_\pm\right)=-S_\gamma\,\left(m_j/m^0\right)^{1/2}$$

By definition

$$\mathrm{S_V=\left[\partial S_\gamma/\partial p\right]_T}$$

Then [1],

$$\mathrm{T\,\left[\partial\ln\left(\gamma_\pm\right)/\partial p\right]_T=-T\,S_v\,\left(m_j/m^0\right)^{1/2}}$$

Hence we write [2]

$$\mathrm{E_{pj}(aq)=E_{pj}^\infty(aq)-v_j\,R\,S_{Ep}\,\left(m_j/m^0\right)^{1/2}}$$

where [3],

$$\mathrm{S_{Ep}=S_V+T\,\left[\partial S_V/\partial T\right)_p}$$

Therefore a linear dependence of $\mathrm{E_{pj}(aq)}$ on $\left(\mathrm{m_j/m^0}\right)^{1/2}$ for dilute solutions is predicted by the DHLL. Hence for dilute solutions

$$\phi\left(E_{pj}\right)=\phi\left(E_{pj}\right)^\infty-(2/3)\,v\,R\,S_{Ep}\,\left(m_j/m^0\right)^{1/2}$$

For tetra-alkylammonium iodides(aq) $\left[\partial\phi\left(\mathrm{V_j}\right)^\infty/\partial\mathrm{T}\right]_\mathrm{p}$ is positive, the magnitude increasing on going from $\mathrm{Me_4N^+}$ to $\mathrm{Bu_4N^+}$ [4,5,].

Apparent molar isobaric expansions for divalent metal chlorides(aq) lead to estimates of ionic molar isobaric expansions based on $\mathrm{E_p^\infty\left(Cl^-;aq\right)}$ set at $+0.046\ \mathrm{cm^3\ mol^{-1}\ K^{-1}}$ [6,7]. The ionic estimates show a linear dependence on $\left(\mathrm{r_j}\right)^{-1}$, a pattern predicted by the Born equation. $\phi\left(\mathrm{E_{pj}}\right)^\infty$ for $\mathrm{NaBPh_4}$ decreases gradually over the range 0 to 60 Celsius [8].

$\phi\left(E_{pj}\right)^\infty$ for $\mathrm{NaF(aq)}$, $\mathrm{Na_2SO_4(aq)}$ and $\mathrm{KCl(aq)}$ is positive [9].

Footnotes

[1]

$$S_\gamma = [1] \quad S_V = \left[Nm^{-2}\right]^{-1} \qquad T\,S_V = [K]\,\left[Nm^{-2}\right]^{-1}$$
$$\left\{\left[\partial \ln(\gamma_\pm)/\partial p\right]_T + T\,\left[\partial^2 \ln(\gamma_\pm)/\partial p\,\partial T\right]\right\}$$
$$= \left\{\left[Nm^{-2}\right]^{-1} + [K]\,[1]\,\left[Nm^{-2}\right]^{-1}\,[K]^{-1}\right\} = \left[Nm^{-2}\right]^{-1}$$

[2]

$$\left[m^3\ mol^{-1}\ K^{-1}\right] = \left[m^3\ mol^{-1}\ K^{-1}\right] - [1]\,\left[JK^{-1}\ mol^{-1}\right]\,\left[Nm^{-2}\right]^{-1}$$
$$= \left[m^3\ mol^{-1}\ K^{-1}\right] - \left[m^3\ mol^{-1}\ K^{-1}\right]$$

[3] $S_{Ep} = \left[Nm^{-2}\right]^{-1} + [K]\,\left[Nm^{-2}\right]^{-1}\,\left[K^{-1}\right] = \left[Nm^{-2}\right]^{-1}$

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1.12.13: Expansions- Isobaric- Binary Liquid Mixtures

The isobaric (equilibrium) expansion of a liquid, volume V, is defined by equation (a).

$$\mathrm{E_p} = \left(\frac{\partial V}{\partial T}\right)_p$$

Both $\mathrm{E_p}$ and V are extensive properties of a mixture. Therefore it is convenient to refer to the molar property, $\mathrm{E_{pm}(mix)}$. Thus

$$\mathrm{E_{pm}(mix)} = \left(\frac{\partial \mathrm{V_m(mix)}}{\partial \mathrm{T}}\right)_\mathrm{p}$$

At fixed T and p, $\mathrm{V_m(mix)}$ for a binary liquid mixture is related to the partial molar volumes of the two components.

$$\mathrm{V_m(mix)} = \mathrm{x_1\,V_1(mix) + x_2\,V_2(mix)}$$

From equation (b)

$$\mathrm{E_{pm}(mix)} = \mathrm{x_1}\left(\frac{\partial \mathrm{V_1(mix)}}{\partial \mathrm{T}}\right)_\mathrm{p} + \mathrm{x_2}\left(\frac{\partial \mathrm{V_2(mix)}}{\partial \mathrm{T}}\right)_\mathrm{p}$$

For a binary mixture having molar volume $\mathrm{V_m(mix)}$ and density $\rho(\mathrm{mix})$,

$$\rho(\mathrm{mix}) = \left(\mathrm{x_1\,M_1 + x_2\,M_2}\right)/\mathrm{V_m(mix)}$$

Here $\mathrm{M_1}$ and $\mathrm{M_2}$ are the molar masses of liquids 1 and 2 respectively.

$$\mathrm{V_m(mix)} = \left(\mathrm{x_1\,M_1 + x_2\,M_2}\right)/\rho(\mathrm{mix})$$

Hence,

$$\left[\partial \mathrm{V_m(mix)}/\partial \mathrm{T}\right]_\mathrm{p} = - \left[\left(\mathrm{x_1\,M_1 + x_2\,M_2}\right)/\rho(\mathrm{mix})\right]\left[\partial \ln\{\rho(\mathrm{mix})\}/\partial \mathrm{T}\right]_\mathrm{p}$$

$mathrmE_{\mathrm{pm}}(\mathrm{mix})$ is obtained for a given mixture from the isobaric dependence of density on temperature. There is merit in considering equations for $\mathrm{E_{pm}(mix;\,id)}$ of a binary mixture having ideal thermodynamic properties and hence for the related excess molar expansion $\mathrm{E^E_{pm}}$. With,

$$\mathrm{E_{pm}(mix;\,id)} = \mathrm{x_1\,E^*_1}(\ell) + \mathrm{x_2\,E^*_2}(\ell)$$

$$\mathrm{E^E_{pm}} = \mathrm{E_{pm}(mix)} - \mathrm{E_{pm}(mix;\,id)}$$

$\mathrm{E_{pm}(mix;\,id)}$ is the mole fraction weighted sum of the isobaric expansions of the pure liquid components at the same T and p. The isobaric expansibility of an ideal binary liquid mixture $\alpha_p(\mathrm{mix;\,id})$ is given by equation (j).

$$\alpha_\mathrm{p}(\mathrm{mix;\,id}) = \frac{\mathrm{x_1\,E^*_{p1}}(\ell) + \mathrm{x_2\,E^*_{p2}}(\ell)}{\mathrm{x_1\,V^*_1}(\ell) + \mathrm{x_2\,V^*_2}(\ell)}$$

Or,

$$\alpha_\mathrm{p}(\mathrm{mix;\ id}) = \frac{\mathrm{x_1\,E^*_{p1}}(\ell)}{\mathrm{x_1\,V^*_1}(\ell) + \mathrm{x_2\,V^*_2}(\ell)} + \frac{\mathrm{x_2\,E^*_{p2}}(\ell)}{\mathrm{x_1\,V^*_1}(\ell) + \mathrm{x_2\,V^*_2}(\ell)}$$

Hence,

$$\alpha_\mathrm{p}(\mathrm{mix;\,id}) = \frac{\mathrm{x_1\,V^*_1}(\ell)\,\alpha^*_{\mathrm{p1}}(\ell)}{\mathrm{x_1\,V^*_1}(\ell) + \mathrm{x_2\,V^*_2}(\ell)} + \frac{\mathrm{x_2\,V^*_2}(\ell)\,\mathrm{E^*_{p2}}(\ell)}{\mathrm{x_1\,V^*_1}(\ell) + \mathrm{x_2\,V^*_2}(\ell)}$$

Hence, expansibility $\alpha_p(\mathrm{mix;\,1\ d})$ can be expressed in terms of the volume fractions of the corresponding ideal binary liquid mixture.

$$\alpha_p(\mathrm{mix;\ id}) = \phi_1(\mathrm{mix;\ id})\,\alpha^*_{p1}(\ell) + \phi_2(\mathrm{mix;\ id})\,\alpha^*_{p2}(\ell)$$

The excess (equilibrium) isobaric expansivity $\alpha_p^E(\mathrm{mix})$ is given by mix equation (n) [1].

$$\alpha_{\mathrm{p}}^{\mathrm{E}}(\mathrm{mix}) = \frac{1}{\mathrm{V_m(mix)}} \left[\left(\frac{\partial \mathrm{V_m^E(mix)}}{\partial \mathrm{T}} \right)_{\mathrm{p}} - \mathrm{V_m^E}\, \alpha_{\mathrm{p}}(\mathrm{mix;id}) \right]$$

From another standpoint the thermal expansion of a binary liquid mixture is analysed in terms of the differential dependence of rational activity coefficients on temperature and pressure. For liquid component 1 at temperature T and pressure p,

$$\mu_1(\mathrm{mix}) = \mu_1^0(\ell) + \mathrm{R\,T\ ln\,(x_1\,f_1)} + \int_{\mathrm{p}}^{\mathrm{p}} \mathrm{V_1^*}(\ell)\,\mathrm{dp}$$

Then

$$\mathrm{V_1(mix)} = \mathrm{V_1^*}(\ell) + \mathrm{R\,T}\ [\partial \ln(\mathrm{f_1})/\partial \mathrm{p}]_{\mathrm{T}}$$

At temperature T,

$$\mathrm{E_{p_1}(mix)} = \mathrm{E_{p1}(mix;id)} + \mathrm{R}\ [\partial \ln(\mathrm{f_1})/\partial \mathrm{p}]_{\mathrm{T}} + \mathrm{R\,T}\ \left[\frac{\partial}{\partial \mathrm{T}} \left(\frac{\partial \ln(\mathrm{f_1})}{\partial \mathrm{p}} \right)_{\mathrm{T}} \right]_{\mathrm{p}}$$

$$\mathrm{E_{p2}(mix)} = \mathrm{E_{p2}(mix;id)} + \mathrm{R}\ [\partial \ln(\mathrm{f_2})/\partial \mathrm{p}]_{\mathrm{T}} + \mathrm{R\,T}\ \left[\frac{\partial}{\partial \mathrm{T}} \left(\frac{\partial \ln(\mathrm{f_2})}{\partial \mathrm{p}} \right)_{\mathrm{T}} \right]_{\mathrm{p}}$$

Two equations follow for the excess partial molar isobaric expansions of the components of the mixture.

$$\mathrm{E_{p1}^E(mix)} = \mathrm{R}\ [\partial \ln(\mathrm{f_1})/\partial \mathrm{p}]_{\mathrm{T}} + \mathrm{R\,T}\ \left[\frac{\partial}{\partial \mathrm{T}} \left(\frac{\partial \ln(\mathrm{f_1})}{\partial \mathrm{p}} \right)_{\mathrm{T}} \right]_{\mathrm{p}}$$

$$E_{\mathrm{p2}}^{\mathrm{E}}(\mathrm{mix}) = \mathrm{R}\ \left[\partial \ln(\mathrm{f_2})/\partial \mathrm{p_T} + \mathrm{R\,T}\ \left[\frac{\partial}{\partial \mathrm{T}} \left(\frac{\partial \ln(\mathrm{f_2})}{\partial \mathrm{p}} \right)_{\mathrm{T}} \right]_{\mathrm{p}} \right.$$

Therefore for the mixture,

$$\mathrm{E_{pm}^E(mix)} = \mathrm{x_1\,E_{p1}^E(mix)} + \mathrm{x_2\,E_{p2}^E(mix)}$$

Footnotes

[1] For a binary liquid mixture at defined T and p,

$$\mathrm{V_m(mix)} = \mathrm{V_m(mix;id)} + \mathrm{V_m^E}$$

$$\alpha_p(\mathrm{mix}) = \frac{1}{V_m(\mathrm{mix})} \frac{\partial}{\partial T} \left[V_m(\ \mathrm{mix}\ ;1\ \mathrm{d}) + V_m^E \right]$$

Or, $\alpha_p(\mathrm{mix}) = \frac{1}{V_m(\mathrm{mix})} \frac{\partial \mathrm{V_m(mix;id)}}{\partial \mathrm{T}} + \frac{1}{\mathrm{V_m(mix)}} \frac{\partial \mathrm{V_m^E}}{\partial \mathrm{T}}$

But, $\alpha_p(\mathrm{mix;id}) = \frac{1}{\mathrm{V_m(mix;id)}} \frac{\partial \mathrm{V_m(mix;id)}}{\partial \mathrm{T}}$

By definition,

$$\alpha_p^E = \alpha_p(\mathrm{mix}) - \alpha_p(\mathrm{mix;\ id}\ )$$

$$\alpha_p^E(\mathrm{mix}) = \left[\frac{1}{V_m(\mathrm{mix})} - \frac{1}{V_m(\mathrm{mix};i\ \mathrm{d})} \right] \frac{\partial V_m(\mathrm{mix;id})}{\partial \mathrm{T}} + \frac{1}{\mathrm{V_m(mix)}} \frac{\partial \mathrm{V_m^E}}{\partial \mathrm{T}}$$

$$\alpha_p^{\mathrm{E}}(\mathrm{mix}) = \left[\frac{\mathrm{V_m(mix;id)} - \mathrm{V_m(mix)}}{\mathrm{V_m(mix)\,V_m(mix;id)}} \right] \frac{\partial \mathrm{V_m(mix;id)}}{\partial \mathrm{T}} + \frac{1}{\mathrm{V_m(mix)}} \frac{\partial \mathrm{V_m^E}}{\partial \mathrm{T}}$$

$$\alpha_{\mathrm{p}}^{\mathrm{E}}(\mathrm{mix}) = -\left[\frac{\mathrm{V_m^E}}{\mathrm{V_m(mix)}} \right] \alpha_{\mathrm{p}}(\mathrm{mix;id}) + \frac{1}{\mathrm{V_m(mix)}} \frac{\partial \mathrm{V_m^E}}{\partial \mathrm{T}}$$

Hence,

$$\alpha_p^E(\mathrm{mix}) = \frac{1}{V_m(\mathrm{mix})} \left[\left(\frac{\partial V_m^E}{\partial T} \right)_p - V_m^E\, \alpha_p(\mathrm{mix;\ id}\ ) \right]$$

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1.12.14: Expansibilities- Isobaric- Binary Liquid Mixtures

A given binary liquid mixture is prepared using liquids 1 and 2 at defined T and p. The molar volume of this mixture is given by equation (a). In the event that thermodynamic properties of the mixture are ideal, the molar volume is given by equation (a).

$$\mathrm{V_m(mix;id)} = \mathrm{x_1\,V_1^*}(\ell) + \mathrm{x_2\,V_2^*}(\ell)$$

At fixed pressure,

$$\left(\frac{\partial \mathrm{V_m(mix;id)}}{\partial \mathrm{T}}\right)_\mathrm{p} = \mathrm{x_1}\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p} + \mathrm{x_2}\left(\frac{\partial \mathrm{V_2^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p}$$

$$\frac{\mathrm{V_m(mix;id)}}{\mathrm{V_m(mix;id)}}\left(\frac{\partial \mathrm{V_m(mix;id)}}{\partial \mathrm{T}}\right)_\mathrm{p} = \mathrm{x_1}\frac{\mathrm{V_1^*}(\ell)}{\mathrm{V_1^*}(\ell)}\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p} + \mathrm{x_2}\frac{\mathrm{V_2^*}(\ell)}{\mathrm{V_2^*}(\ell)}\left(\frac{\partial \mathrm{V_2^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p}$$

Hence,

$$\mathrm{V_m(mix;id)}\,\alpha_\mathrm{p}(\mathrm{mix;id}) = \mathrm{x_1\,V_1^*}(\ell)\,\alpha_{\mathrm{p1}}^*(\ell) + \mathrm{x_2\,V_2^*}(\ell)\,\alpha_{\mathrm{p2}}^*(\ell)$$

But

$$\phi_1(\mathrm{mix;id}) = \mathrm{x_1\,V_1^*}(\ell)/\mathrm{V_m(mix;id)}$$

And,

$$\phi_2(\mathrm{mix;id}) = \mathrm{x_2\,V_2^*}(\ell)/\mathrm{V_m(mix;id)}$$

Hence

$$\alpha_p(\mathrm{mix;\ id\ }) = \phi_1(\mathrm{mix;\ id\ })\,\alpha_{p1}^*(\ell) + \phi_2(\mathrm{mix;\ id\ })\,\alpha_{p2}^*(\ell)$$

For a real binary liquid mixture,

$$\mathrm{V_m(mix)} = \mathrm{x_1\,V_1^*}(\ell) + \mathrm{x_2\,V_2^*}(\ell) + \mathrm{V_m^E(mix)}$$

At fixed pressure,

$$\left(\frac{\partial \mathrm{V_m(mix)}}{\partial \mathrm{T}}\right)_\mathrm{p} = \mathrm{x_1}\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p} + \mathrm{x_2}\left(\frac{\partial \mathrm{V_2^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p} + \left(\frac{\partial \mathrm{V_m^E}}{\partial \mathrm{T}}\right)_\mathrm{p}$$

Or,

$$\frac{\mathrm{V_m(mix)}}{\mathrm{V_m(mix)}}\left(\frac{\partial \mathrm{V_m(mix)}}{\partial \mathrm{T}}\right)_\mathrm{p} = \mathrm{x_1}\frac{\mathrm{V_1^*}(\ell)}{\mathrm{V_1^*}(\ell)}\left(\frac{\partial \mathrm{V_1^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p} + \mathrm{x_2}\frac{\mathrm{V_2^*}(\ell)}{\mathrm{V_2^*}(\ell)}\left(\frac{\partial \mathrm{V_2^*}(\ell)}{\partial \mathrm{T}}\right)_\mathrm{p} + \left(\frac{\partial \mathrm{V_m^E}}{\partial \mathrm{T}}\right)_\mathrm{p}$$

$$\mathrm{V_m(mix)}\,\alpha_\mathrm{p}(\mathrm{mix}) = \mathrm{x_1\,V_1^*}(\ell)\,\alpha_{\mathrm{p1}}^*(\ell) + \mathrm{x_2\,V_2^*}(\ell)\,\alpha_{\mathrm{p2}}^*(\ell) + \left(\frac{\partial \mathrm{V_m^E}}{\partial \mathrm{T}}\right)_\mathrm{p}$$

Or,

$$\alpha_p(\mathrm{mix}) = \frac{1}{V_\mathrm{m}(\mathrm{mix})}\left[x_1\,V_1^*(\ell)\,\alpha_{p1}^*(\ell) + x_2\,V_2^*(\ell)\,\alpha_{p2}^*(\ell) + \left(\frac{\partial V_m^E}{\partial T}\right)_p\right]$$

We may also define an excess property using equation (k) but it is important to note that $\alpha_\mathrm{p}^\mathrm{E}$ is not a simple second derivative of the excess molar Gibbs energy, $\mathrm{G_m^E}$.

$$\alpha_p^E(\mathrm{mix}) = \alpha_p(\mathrm{mix}) - \alpha_p(\mathrm{mix;\ id\ })$$

We start out using an alternative expression for $\alpha_p(\text{mix})$.

$$\alpha_p(\text{mix}) = \frac{1}{V_m(\text{mix})}\left[V_m(\text{mix;id})\,\alpha_p(\text{mix;id}) + \left(\frac{\partial \text{V}_\text{m}^E}{\partial T}\right)_\text{p}\right]$$

$$\alpha_p^E(\text{mix}) = \frac{1}{V_m(\text{mix})}\left[V_m(\text{mix;\ id\ })\,\alpha_p(\text{mix;id}) + \left(\frac{\partial V_m^E}{\partial T}\right)_p\right] - \alpha_p(\text{mix;\ id\ })$$

$$\alpha_\text{p}^\text{E}(\text{mix}) = \frac{1}{\text{V}_\text{m}(\text{mix})}\left[\left(\frac{\partial \text{V}_\text{m}^\text{E}}{\partial \text{T}}\right)_\text{p} + [\text{V}_\text{m}(\text{mix;id}) - \text{V}_\text{m}(\text{mix})]\ \alpha_\text{p}(\text{mix;id}]\right.$$

Hence, [1]

$$\alpha_p^E(\text{mix}) = \frac{1}{V_m(\text{mix})}\left[\left(\frac{\partial V_m^E}{\partial T}\right)_p - V_m^E(\text{mix})\,\alpha_p(\text{\ mix\ ;\ id\ }]\right.$$

Footnotes

[1]

$$\alpha_\text{p}^\text{E}(\text{mix}) = [\text{K}^{-1}]$$

$$\left[\left(\frac{\partial \text{V}_\text{m}^\text{E}}{\partial \text{T}}\right)_\text{p} - \text{V}_\text{m}^\text{E}\,\alpha_\text{p}(\text{mix;id})\right] = \frac{[\text{m}^3\ \text{mol}^{-1}]}{[\text{K}]} - [\text{m}^3\ \text{mol}^{-1}]\ [\text{K}^{-1}] = [\text{m}^3\ \text{mol}^{-1}\ \text{K}^{-1}]$$

$$\frac{1}{V_m(mix)}\left[\left(\frac{\partial V_m^E}{\partial T}\right)_p - V_m^E\,\alpha_p(\text{\ mix\ ;}id)\right]$$

$$= \frac{1}{[\ \text{m}^3\ \text{mol}^{-1}]}\ [\text{m}^3\ \text{mol}^{-1}\quad \text{K}^{-1}] = [\text{K}^{-1}]$$

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1.12.15: Expansions- Isentropic- Solutions

The Gibbs energy of a closed system at thermodynamic equilibrium containing two chemical substances is defined by equation (a) where the molecular composition/organisation is signalled by ξ^{eq}.

$$G = G\left[T, p, n_1, n_2,\ A = 0, \xi^{eq}\right]$$

$$V = V\left[T, p, n_1, n_2,\ A = 0, \xi^{eq}\right]$$

$$S = S\left[T, p, n_1, n_2,\ A = 0, \xi^{eq}\right]$$

A common feature is the use of the two intensive variables, temperature and pressure, in the definition of extensive properties G, V and S. The properties G, V and S are Gibbsian.

The system is perturbed by an increase in temperature along a path such that the affinity for spontaneous change remains zero and the entropy remains equal to that defined by equation (c). In principle we plot volume V as a function of temperature at constant n_1, n_2, at 'A = 0' and at a constant entropy equal to that defined by equation (c). The gradient of the plot at the point where the volume is defined by equation (b) yields the equilibrium isentropic expansion, $E_S(A = 0)$ [1]; equation (d); isentropic = adiabatic and at equilibrium.

$$E_S(A = 0) = (\partial V/\partial T)_{S.A=0}$$

$E_S(A = 0)$ characterises the system defined by the Gibbsian set of independent variables $[T, p, n_1, n_2,\ A = 0, \xi^{eq}]$. As we change the amount of solute n_j for a fixed temperature, pressure and amount of solvent n_1, so both $V(aq)$ and $S(aq)$ change yielding a new isentropic thermal expansion $E_S(aq)$ at a new entropy $S(aq)$. For a series of solutions having different molalities, comparison of $E_S(aq)$ is not straightforward because entropy $S(aq)$ is itself a function of solution composition. Further comparison cannot be readily drawn with the isentropic thermal expansion of the pure solvent $E^*_{Sl}(\ell)$ equation (e).

$$E^*_{S1}(\ell; A = 0) = (\partial V^*_1(\ell)/\partial T)_{A=0} \text{ at constant } S^*_1(\ell)$$

$E_S(A = 0; aq)$ is a non-Gibbsian property [2]. Consequently, familiar thermodynamic relationships involving partial molar properties are not valid in the case of partial molar isentropic (thermal) expansions which are non-Lewisian properties [2,3]. $[\partial V_j(aq)/\partial T]$ for solute-j in aqueous solution at constant $S(aq)$ is a semi-partial molar property [4].

For an aqueous solution having entropy $S(aq)$, two partial molar isentropic expansions are defined for the solvent and solute. At $S(aq)$ characterised by T, p, n_1 and n_j,

$$E_{Sl}(aq; def) = [\partial E_S(aq)/\partial n_1] \text{ at fixed } T, p and n_j$$

and

$$E_{Sj}(aq; def) = [\partial E_S(aq)/\partial n_j] \text{ at fixed } T, p \text{ and } n_1$$

So that,

$$E_S(aq) = n_1 E_{Sl}(aq; def) + n_j E_{Sj}(aq;\ def\ )$$

Equation (h) relates $E_S(aq)$ to the partial molar intensive isentropic properties of both solvent and solute.

A similar problem is encountered in defining an apparent molar isentropic expansion for solute-j, $\phi(E_{Sjj})$. We might assert that $\phi(E_{Sjj})$ is defined by the isentropic differential dependence $\phi(V_j)$ on temperature. Alternatively, we use an equation by analogy to those used to relate, for example, $V(aq)$ to $V_1^*(\ell)$ and $\phi(V_j)$. Equation (i) relates $V(aq)$ to the apparent molar volume of solute j, φ(Vj).

$$V(aq) = n_1 V^*_1(\ell) + n_j \phi(V_j)$$

Differentiation of equation (i) at constant entropy again raises the problem that the molar entropy $S(aq)$ does not equal the molar entropy of the pure solvent, $S_1^*(\ell)$. However, by analogy with the definition of $\phi(K_{Sj}; def)$ we define a quantity $\phi(E_{Sj};\ def\ )$ using equation (j).

$$E_s(aq) = n_1 E^*_{Sl}(\ell) + n_j \phi(E_{Sj}; def)$$

$\mathrm{E}^*_{\mathrm{Sl}}(\ell)$ is the molar intensive property of the solvent. The isentropic expansion of the solution at entropy $\mathrm{S(aq)}$ is linked with that of the pure solvent at entropy $\mathrm{S}^*_1(\ell)$. Further [5]

$$\phi\left(E_{sj};\mathrm{def}\right)=\left[\mathrm{m_j}\,\rho^*_1(\ell)\right]^{-1}\,\left[\alpha_s(\mathrm{aq})-\alpha^*_{s1}(\ell)\right]+\alpha_s(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$

$$\phi\left(E_{\mathrm{sj}};\ \mathrm{def}\ \right)=\left[\alpha_s(\mathrm{aq})-\alpha^*_{s1}(\ell)\right]\,\left(\mathrm{c_j}\right)^{-1}+\alpha^*_{s1}(1)\,\phi\left(\mathrm{V_j}\right)$$

Footnotes

[1] From $\left(\frac{\partial^2 \mathrm{U}}{\partial S\,\partial V}\right)=\left(\frac{\partial^2 \mathrm{U}}{\partial V\,\partial S}\right),\quad \left(\frac{\partial \mathrm{T}}{\partial V}\right)_s=-\left(\frac{\partial \mathrm{p}}{\partial S}\right)_{\mathrm{V}}$ We invert the latter equation. Hence, $E_S=\left(\frac{\partial V}{\partial T}\right)_s=-\left(\frac{\partial S}{\partial p}\right)_V$

The isentropic dependence of volume on temperature equals (with reversed sign) the isochoric dependence of entropy on pressure.

[2] J. C. R. Reis, M. J. Blandamer, M. I. Davis and G. Douheret., Phys. Chem. Chem. Phys.,2001,**3**,1465.

[3] J. C. R. Reis, J. Chem. Soc. Faraday Trans. 2,1982,**78**,1595.

[4] M. J. Blandamer, M. I. Davis, G. Douheret and J. C. R. Reis., Chem. Soc. Rev., 2001,**30**,8.

[5] From

$$\phi\left(E_{\mathrm{S}j};\ \mathrm{def}\ \right)=\frac{E_{\mathrm{S}}\left(\mathrm{aq};\mathrm{w}_1=1\ \mathrm{kg}\right)-\left(1/\mathrm{M}_1\right)\,\mathrm{E}^*_{\mathrm{S}1}(\ell)}{\mathrm{m_j}}$$

$$\phi\left(\mathrm{E_{Sj}};\ \mathrm{def}\ \right)=\frac{\mathrm{E_S}\left(\mathrm{aq};\mathrm{w}_1=1\ \mathrm{kg}\right)}{\mathrm{m_j}}-\frac{\mathrm{E}^*_{\mathrm{S}1}(\ell)}{\mathrm{m_j\,M_1}}$$

$$\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right)=\frac{\alpha_s(\mathrm{aq})\,\mathrm{V}\left(\mathrm{aq};\mathrm{w}_1=1\ \mathrm{kg}\right)}{\mathrm{m_j}}-\frac{\alpha^*_{s1}(\ell)\,\mathrm{V}^*_1(\ell)}{\mathrm{m_j\,M_1}}$$

But $\mathrm{V}\left(\mathrm{aq};\mathrm{w}_1/\mathrm{kg}=1\right)=\left(1/\mathrm{M}_1\right)\ \mathrm{V}^*_1(\ell)+\mathrm{m_j}\,\phi\left(\mathrm{V_j}\right)$

Then $\phi\left(\mathrm{E}_{sj};\mathrm{def}\right)=\frac{\alpha_s(\mathrm{aq})\,\left[(1/\mathrm{M}_1)\mathrm{V}^*_1(\ell)+\mathrm{m_j}\,\phi(\mathrm{V_j})\right]}{\mathrm{m_j}}-\frac{\alpha^*_{s1}(\ell)\,\mathrm{V}^*_1(\ell)}{\mathrm{m_j\,M_1}}$

Or, $\phi\left(\mathrm{E_{Sj}};\ \mathrm{def}\ \right)=\frac{\mathrm{V}^*_1(\ell)}{\mathrm{m_j\,M_1}}\,\left[\alpha_s(\mathrm{aq})-\alpha^*_{s1}(\ell)\right]+\alpha_s(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$

Hence, $\phi\left(\mathrm{E_{sj}};\mathrm{def}\right)=\left[\mathrm{m_j}\,\rho^*_1(\ell)\right]^{-1}\,\left[\alpha_s(\mathrm{aq})-\alpha^*_{s1}(\ell)\right]+\alpha_s(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$

But $\frac{1}{\mathrm{m_j}\,\rho^*_1(\ell)}=\frac{1}{\mathrm{c_j}}-\phi\left(\mathrm{V_j}\right)$

Then \phi\left(E_{s j} ; \operatorname{def}\right)=\left[\frac{1}{c_{j}}-\phi\left(V_{j}\right)\right] \,\left[\alpha_{s}(\mathrm{aq})-\alpha_{\mathrm{s}_{1}}^{*}(\ell)\right]+\alpha_{\mathrm{s}}(\mathrm{aq}) \, \phi\left(\mathrm{V}_{\mathrm{j}}\right)\)

Or, $\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right)=\left[\mathrm{c_j}\right]^{-1}\,\left[\alpha_s(\mathrm{aq})-\alpha^*_{s1}(\ell)\right]$
$-\phi\left(\mathrm{V_j}\right)\,\alpha_s(\mathrm{aq})+\phi\left(\mathrm{V_j}\right)\,\alpha^*_{s1}(\ell)+\alpha_s(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$

Hence,

$$\phi\left(\mathrm{E_{sj}};\mathrm{def}\right)=\left[\mathrm{c_j}\right]^{-1}\,\left[\alpha_s(\mathrm{aq})-\alpha^*_{s1}(\ell)\right]+\phi\left(\mathrm{V_j}\right)\,\alpha^*_{s1}(\ell)$$

$$\phi\left(\mathrm{E_{Sj}};\ \mathrm{def}\ \right)=\left[\mathrm{m^3\ K^{-1}\ mol^{-1}}\right]$$

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1.12.16: Expansions- Solutions- Apparent Molar Isentropic and Isobaric

In the context of the properties of aqueous solutions the concept of apparent molar properties is important with respect to the analysis of experimental results; e.g. apparent molar volume for solute j $\phi\left(\mathrm{V_j}\right)$ calculated from the densities of a given solution and solvent at fixed T and p. Similarly apparent molar isobaric expansions $\phi\left(\mathrm{E_{pj}}\right)$ characterise the dependence of \phi\left(\mathrm{V}_{j}\right) on temperature at fixed pressure. Nevertheless problems emerge when we turn attention to comparable isentropic properties. The way ahead involves definition of apparent molar isentropic expansions $\phi\left(\mathrm{E_{sj};\ def}\right)$ and apparent molar isentropic compressions $\phi\left(\mathrm{K_{sj};\ def}\right)$. These two properties are related [1]; equation(a).

$$\begin{aligned}&\phi\left(\mathrm{E_{sj}};\mathrm{def}\right)=\\&-\frac{\alpha^*_{\mathrm{S1}}(\ell)}{\alpha_{\mathrm{p}}(\mathrm{aq})}\,\phi\left(\mathrm{E_{pj}}\right)+\frac{\alpha_{\mathrm{s}}(\mathrm{aq})}{\kappa_{\mathrm{s}}(\mathrm{aq})}\,\phi\left(\mathrm{K_s}\right)+\frac{\alpha_{\mathrm{s}}(\mathrm{aq})\,\kappa^*_{\mathrm{S1}}(\ell)}{\kappa_{\mathrm{s}}(\mathrm{aq})\,\sigma(\mathrm{aq})}\,\phi\left(\mathrm{C_{pj}}\right)\\&+\left[\alpha^*_{\mathrm{p1}}(\ell)\,\left(1+\frac{\alpha^*_{\mathrm{pl1}}(\ell)}{\alpha_{\mathrm{p}}(\mathrm{aq})}\right)-\frac{\alpha_{\mathrm{s}}(\mathrm{aq})\,\kappa^*_{\mathrm{S1}}(\ell)}{\kappa_{\mathrm{s}}(\mathrm{aq})}\,\left(1+\frac{\sigma^*_1(\ell)}{\sigma(\mathrm{aq})}\right)\right]\,\phi\left(\mathrm{V_j}\right)\end{aligned}$$

Equation (b) relates the corresponding properties at infinite dilution [1].

$$\frac{\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right)^{\infty}}{\alpha^*_{\mathrm{S1}}(\ell)}=-\frac{\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\alpha^*_{\mathrm{p1}}(\ell)}+\frac{\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^{\infty}}{\kappa^*_{\mathrm{S1}}(\ell)}+\frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\sigma^*_1(\ell)}$$

‘Semi’ apparent molar isentropic expansions and compressions are related using equation (c)

$$\frac{1}{\alpha_{\mathrm{S}}(\mathrm{aq})}\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial\mathrm{T}}\right]_{\mathrm{S(aq)}}=-\frac{1}{\kappa_{\mathrm{S}}(\mathrm{aq})}\left[\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial\mathrm{p}}\right]_{\mathrm{S(aq)}}$$

Equations (a) , (b) and (c) illustrate the power of thermodynamics in drawing together and relating the several properties of a solution.

Footnotes

[1] In the following we simplify the algebra by omitting the descriptors (aq) and (ℓ). The starting point is the following equation.

$$\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}=\frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}\,\sigma}\,\left(\kappa_{\mathrm{s}}\,\sigma-\kappa^*_{\mathrm{s}}\,\sigma^*\right)-\frac{\alpha^*_{\mathrm{s}}}{\alpha_{\mathrm{p}}}\,\left(\alpha_{\mathrm{p}}-\alpha^*_{\mathrm{p}}\right)$$

The latter equation is effectively an identity. From equation (a),

$$\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}=\alpha_{\mathrm{s}}-\frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}\,\sigma}\,\kappa^*_{\mathrm{s}}\,\sigma^*-\alpha^*_{\mathrm{s}}+\frac{\alpha^*_{\mathrm{s}}}{\alpha_{\mathrm{p}}}\,\alpha^*_{\mathrm{p}}$$

From equation (b), $\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}=\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}+\frac{\kappa_{\mathrm{s}}\,\sigma}{\mathrm{T}\,\alpha_{\mathrm{p}}\,\kappa_{\mathrm{s}}\,\sigma}\,\kappa^*_{\mathrm{s}}\,\sigma^*-\frac{\kappa^*_{\mathrm{S}}\,\sigma^*}{\alpha_{\mathrm{p}}\,\mathrm{T}}$ or, $\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}=\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}$

But as an identity,

$$\kappa_{\mathrm{S}}\,\sigma-\kappa^*_{\mathrm{S}}\,\sigma^*=\sigma\,\left(\kappa_{\mathrm{S}}-\kappa^*_{\mathrm{S}}\right)+\kappa^*_{\mathrm{S}}\,\left(\sigma-\sigma^*\right)$$

From equations (a) and (c). $\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}=\frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}}\,\left(\kappa_{\mathrm{s}}-\kappa^*_{\mathrm{s}}\right)+\frac{\alpha_{\mathrm{s}}\,\kappa^*_{\mathrm{s}}}{\kappa_{\mathrm{s}}\,\sigma}\,\left(\sigma-\sigma^*\right)-\frac{\alpha^*_{\mathrm{s}}}{\alpha_{\mathrm{p}}}\left(\alpha_{\mathrm{p}}-\alpha^*_{\mathrm{p}}\right)$

But,

$$\begin{aligned}&\phi\left(\mathrm{E}_{sj};\ \mathrm{def}\ \right)=\left[\mathrm{c_j}\right]^{-1}\,\left[\alpha_{\mathrm{s}}-\alpha^*_{\mathrm{s}}\right]+\phi\left(\mathrm{V_j}\right)\,\alpha^*_{\mathrm{s}}\\&\phi\left(\mathrm{E_{S_j}};\mathrm{def}\right)=\frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}}\,\frac{1}{\mathrm{c_j}}\,\left(\kappa_{\mathrm{s}}-\kappa^*_{\mathrm{s}}\right)+\frac{\alpha_{\mathrm{s}}\,\kappa^*_{\mathrm{s}}}{\kappa_{\mathrm{s}}\,\sigma}\,\frac{1}{\mathrm{c_j}}\,\left(\sigma-\sigma^*\right)\\&-\frac{\alpha^*_{\mathrm{s}}}{\alpha_{\mathrm{p}}}\,\frac{1}{\mathrm{c_j}}\,\left(\alpha_{\mathrm{p}}-\alpha^*_{\mathrm{p}}\right)+\alpha^*_{\mathrm{s}}\,\phi\left(\mathrm{V_j}\right)\end{aligned}$$

But for the isobaric heat capacities $\phi\left(\mathrm{C_{pj}}\right)=\left[\mathrm{c_j}\right]^{-1}\,\left[\sigma-\sigma^*\right]+\phi\left(\mathrm{V_j}\right)\,\sigma^*$

Also,

$$\phi\left(\mathrm{K}_{sj};\ \mathrm{def}\ \right) = \left[\mathrm{c_j}\right]^{-1}\left[\kappa_\mathrm{s} - \kappa_\mathrm{s}^*\right] + \phi\left(\mathrm{V_j}\right)\kappa_\mathrm{s}^*$$
$$\phi\left(\mathrm{E_{Sj}};\ \mathrm{def}\ \right) = \frac{\alpha_\mathrm{s}}{\kappa_\mathrm{S}}\left[\phi\left(\mathrm{K_{Sj}};\ \mathrm{def}\ \right) - \kappa_\mathrm{s}^*\,\phi\left(\mathrm{V_j}\right)\right]$$

Hence,

$$+\frac{\alpha_\mathrm{s}\,\kappa_\mathrm{s}^*}{\kappa_\mathrm{s}\,\sigma}\left[\phi\left(\mathrm{C_{pj}}\right) - \sigma^*\,\phi\left(\mathrm{V_j}\right)\right]$$
$$-\frac{\alpha_\mathrm{s}^*}{\alpha_\mathrm{p}}\left[\phi\left(\mathrm{E_{pj}}\right) - \alpha_\mathrm{p}^*\,\phi\left(\mathrm{V_j}\right)\right] + \alpha_\mathrm{s}^*\,\phi\left(\mathrm{V_j}\right)$$

With a little reorganisation,

$$\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right) = -\frac{\alpha_\mathrm{S}^*}{\alpha_\mathrm{p}}\,\phi\left(\mathrm{E_{pj}}\right) + \frac{\alpha_\mathrm{S}}{\kappa_\mathrm{S}}\,\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right) + \frac{\alpha_\mathrm{s}\,\kappa_\mathrm{s}^*}{\kappa_\mathrm{S}\,\sigma}\,\phi\left(\mathrm{C_{pj}}\right)$$
$$+\left[\alpha_\mathrm{s}^*\left(1+\frac{\alpha_\mathrm{p}^*}{\alpha_\mathrm{p}}\right) - \frac{\alpha_\mathrm{s}\,\kappa_\mathrm{s}^*}{\kappa_\mathrm{S}}\left(1+\frac{\sigma^*}{\sigma}\right)\right]\phi\left(\mathrm{V_j}\right)$$

Hence in the limit of infinite dilution,

$$\frac{\phi\left(E_{\mathrm{S}j};\mathrm{def}\right)^\infty}{\alpha_\mathrm{s}^*} = -\frac{\phi\left(\mathrm{E_{pj}}\right)^\infty}{\alpha_\mathrm{p}^*} + \frac{\phi\left(\mathrm{K}_{sj};\mathrm{def}\right)^\infty}{\kappa_\mathrm{s}^*} + \frac{\phi\left(\mathrm{C_{pj}}\right)^\infty}{\sigma^*}$$

[2]

$$\frac{\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right)^\infty}{\alpha_\mathrm{s}^*} = \frac{\left[\mathrm{m^3\ mol^{-1}\ K^{-1}}\right]}{\left[\mathrm{K^{-1}}\right]} = \left[\mathrm{m^3\ mol^{-1}}\right]$$
$$\frac{\phi\left(\mathrm{E_{pj}}\right)^\infty}{\alpha_\mathrm{p}^*} = \frac{\left[\mathrm{m^3\ mol^{-1}\ K^{-1}}\right]}{\left[\mathrm{K^{-1}}\right]} = \left[\mathrm{m^3\ mol^{-1}}\right]$$
$$\frac{\phi\left(\mathrm{K_{Sj}};\mathrm{def}\right)^\infty}{\kappa_\mathrm{S}^*} = \frac{\left[\mathrm{m^3\ mol^{-1}/Nm^{-2}}\right]}{\left[\mathrm{Nm^{-2}}\right]^{-1}} = \left[\mathrm{m^3\ mol^{-1}}\right]$$
$$\frac{\phi\left(\mathrm{C_{pj}}\right)^\infty}{\sigma^*} = \frac{\left[\mathrm{Jmol^{-1}}\right]}{\left[\mathrm{Jm^{-3}}\right]} = \left[\mathrm{m^3\ mol^{-1}}\right]$$

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1.12.17: Expansions- Isentropic- Solutions- Apparent and Partial Molar

A given solution is prepared using n_1 moles of solvent (water) and n_j moles of solute j. The volume of the system is defined by equation (a).

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}\right]$$

We consider the case where the closed system is at equilibrium and hence where the affinity for spontaneous change is zero. The entropy of the system (at equilibrium) is defined by the same set of independent variables. Thus

$$\mathrm{S} = \mathrm{S}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}\right]$$

The system is perturbed at constant pressure by a change in temperature. The path followed by the system is such that the affinity for spontaneous change remains at zero (i.e. at equilibrium) and that the entropy of the system $\mathrm{S(aq)}$ remains constant at that given by equation (b).

The equilibrium isentropic expansion of the system is defined by equation (c).

$$\mathrm{E}_\mathrm{s}(\mathrm{A}=0) = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{S(aq)},\mathrm{A}=0}$$

$\mathrm{E}_\mathrm{S}(\mathrm{A}=0)$ is an extensive property of the system. Nevertheless it is convenient to consider an intensive property. For example, $\mathrm{E}_\mathrm{S}\left(\mathrm{aq}; \mathrm{A}=0; \mathrm{w}_1 = 1 \text{ kg}; \mathrm{m}_\mathrm{j}\right)$ is the equilibrium isentropic expansion of a solution molality m_j prepared using 1 kg of water(ℓ).

For a system comprising pure solvent at defined T and p we define a molar (equilibrium) isentropic expansion, $\mathrm{E}^*_\mathrm{S}(\ell)$; equation (d).

$$\mathrm{E}^*_{\mathrm{S}1}(\ell; \mathrm{A}=0) = \left(\frac{\partial \mathrm{V}^*_1(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{s}^*_1(\ell),\mathrm{A}=0}$$

The volume of a solution, molality m_j, prepared using 1 kg of water(ℓ) is related to the composition using either equations (e) or (f).

$$\mathrm{V}\left(\mathrm{aq}; \mathrm{w}_1 = 1 \text{ kg}\right) = (1/\mathrm{M}_1)\ \mathrm{V}^*_1(\ell) + \mathrm{m}_\mathrm{j}\, \phi\left(\mathrm{V}_\mathrm{j}\right)$$

$$\mathrm{V}\left(\mathrm{aq}; \mathrm{w}_1 = 1 \text{ kg}\right) = (1/\mathrm{M}_1)\ \mathrm{V}_1(\mathrm{aq}) + \mathrm{m}_\mathrm{j}\, \mathrm{V}_\mathrm{j}(\mathrm{aq})$$

A key problem emerges. We note that the conditions on the partial differential in equation (c) relate to the entropy of the aqueous solution. The latter condition is not the same as that invoked in equation (d) which refers to the molar entropy of the pure solvent. We could of course differentiate equation (e) with respect to temperature at fixed entropy S(aq). However we would encounter a term $\left(\frac{\partial \mathrm{V}^*_1(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{s(aq)}}$. This is a complicated derivative where we might have hoped for a term $\left(\frac{\partial \mathrm{V}^*_1(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{s}^*_1(\ell)}$. The way forward is to accept the problem and define a property, by analogy with the corresponding isobaric property, a property $\phi\left(\mathrm{E}_{\mathrm{S}j};\ \mathrm{def}\ \right)$ which has the appearance of proper thermodynamic apparent property. Then,

$$\mathrm{E}_\mathrm{S}\left(\mathrm{aq}; \mathrm{A}=0; \mathrm{w}_1 = 1 \text{ kg}\right) = (1/\mathrm{M}_1)\ \mathrm{E}^*_{\mathrm{Sl}}(\ell; \mathrm{A}=0) + \mathrm{m}_\mathrm{j}\, \phi\left(\mathrm{E}_{\mathrm{Sj}}; \mathrm{def}\right)$$

There is a subtle problem with respect to equation (f) which can be differentiated with respect to T at constant $\mathrm{S(aq)}$ as defined by equation (b). Then

$$\mathrm{E}_\mathrm{s}\left(\mathrm{aq}; \mathrm{w}_1 = 1 \text{ kg}\right) = (1/\mathrm{M}_1)\left(\frac{\partial \mathrm{V}_1(\mathrm{aq})}{\partial \mathrm{T}}\right)_{\mathrm{S(aq)}} + \mathrm{m}_\mathrm{j}\left(\frac{\partial \mathrm{V}_\mathrm{j}(\mathrm{aq})}{\partial \mathrm{T}}\right)_{\mathrm{S(aq)}}$$

Partial molar isentropic expansions $\mathrm{E}_{\mathrm{S}1}(\mathrm{aq})$ and $\mathrm{E}_{\mathrm{S}j}(\mathrm{aq})$ are defined by the following equations.

$$\mathrm{E}_{\mathrm{Sl}}(\mathrm{aq}) = \left(\frac{\partial \mathrm{E}_\mathrm{s}(\mathrm{aq})}{\partial \mathrm{n}_1}\right)_{\mathrm{T,p,n(j)}}$$

$$\mathrm{E}_{\mathrm{Sj}}(\mathrm{aq}) = \left(\frac{\partial \mathrm{E}_\mathrm{j}(\mathrm{aq})}{\partial \mathrm{n}_\mathrm{j}}\right)_{\mathrm{T,p,n(1)}}$$

But $\mathrm{E}_{\mathrm{S}1}$ and $\mathrm{E}_{\mathrm{S}j}$ are non-Lewisian partial molar properties. Hence

$$\mathrm{E_{Sl}(aq)} \neq \left(\frac{\partial \mathrm{V_1(aq)}}{\partial \mathrm{T}}\right)_{\mathrm{S(aq)}}$$

$$\mathrm{E_{S}}_{j}\mathrm{(aq)} = \left(\frac{\partial \mathrm{V_j(aq)}}{\partial \mathrm{T}}\right)_{\mathrm{s(aq)}}$$

Then,

$$\mathrm{E_S\ (aq;\, w_1 = 1\ kg)} = (1/\mathrm{M_1})\ \mathrm{E_{S1}(aq)} + \mathrm{m_j\, E_{Sj}(aq)}$$

In practical terms equation (n) follows from equation (g),

$$\phi\,(\mathrm{E_{Sj}; def}) = (1/\mathrm{m_j})\ [\mathrm{E_S\ (aq;\, A = 0;\, w_1 = 1\ kg)} - (1/\mathrm{M_1})\ \mathrm{E^*_{S1}}(\ell; \mathrm{A} = 0)]$$

Two practical equations follow from equation (n) allowing $\phi\,(\mathrm{E_{Sj}; def})$ to be calculated from the isentropic expansibilities of solutions and solvent, both volume intensive variables [1].

$$\phi\,(\mathrm{E}_{sj}\mathrm{; def}) = [\mathrm{m_j}\,\rho^*_1(\ell)]^{-1}\ [\alpha_s\mathrm{(aq)} - \alpha^*_{\mathrm{sl}}(\ell)] + \alpha_s\mathrm{(aq)}\,\phi\,(\mathrm{V_j})$$

$$\phi\,(E_{\mathrm{Sj}};\ \mathrm{def}\ ) = [c_j]^{-1}\ [\alpha_s\mathrm{(aq)} - \alpha^*_{\mathrm{s1}}(\ell)] + \alpha^*_{\mathrm{S1}}(\ell)\,\phi\,(\mathrm{V_j})$$

where

$$\alpha_s\mathrm{(aq)} = \frac{1}{\mathrm{V(aq)}}\left(\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right)_{\mathrm{s(aq)}}$$

$$\alpha^*_{\mathrm{S1}}(\ell) = \frac{1}{\mathrm{V^*_1}(\ell)}\left(\frac{\partial \mathrm{V^*_1}(\ell)}{\partial \mathrm{T}}\right)_{\mathrm{s^*_1}(\ell)}$$

Footnotes

[1] From equation (n),

$$\phi\,(\mathrm{E_{Sj}; def}) = (1/\mathrm{m_j})\ [\mathrm{E_s\ (aq;\, w_1 = 1\ kg)} - (1/\mathrm{M_1})\ \mathrm{E^*_{sl}}(\ell)]$$

We use equation (m) for a solution prepared using 1 kg of water.

$$\mathrm{E_s\ (aq;\, w_1 = 1\ kg)} = (1/\mathrm{M_1})\ \mathrm{E_{S1}(aq)} + \mathrm{m_j\, E_{Sj}(aq)}$$

Then

$$\phi\,(\mathrm{E}_{Sj}\mathrm{; def}) = (1/\mathrm{m_j})\ [(1/\mathrm{M_1})\ \mathrm{E_{S1}(aq)} + \mathrm{m_j\, E_{Sj}(aq)} - (1/\mathrm{M_1})\ \mathrm{E^*_{Sl1}}(\ell)]$$

Or,

$$\phi\,(\mathrm{E}_{sj}\mathrm{; def}) = \mathrm{E}_{Sj}\mathrm{(aq)} + (1/\mathrm{M_1})\ (1/\mathrm{m_j})\ [\mathrm{E_{Sl}(aq)} - \mathrm{E^*_{s1}}(\ell)]$$

Hence using equation (m),

$$\phi\,(\mathrm{E_{Sj}; def}) = (1/\mathrm{m_j})\ \mathrm{E_s\ (aq;\, w_1 = 1\ kg)} - (1/\mathrm{M_1})\ (1/\mathrm{m_j})\ \mathrm{E^*_{Sl}}(\ell)$$

Using equations (q) and (r),

$$\phi\,(\mathrm{E_s; def}) = (1/\mathrm{m_j})\ \alpha_s\mathrm{(aq)\,V\,(aq;\, w_1 = 1\ kg)} - (1/\mathrm{M_1})\ (1/\mathrm{m_j})\ \alpha^*_{\mathrm{s1}}(\ell)\,\mathrm{V^*_1}(\ell)$$

Or,

$$\begin{aligned}\phi\,(\mathrm{E}_{sj}\mathrm{;\ def}\ ) =& (1/\mathrm{m_j})\ \alpha_s\mathrm{(aq)}\ [(1/\mathrm{M_1})\,\mathrm{V^*_1}(\ell) + \mathrm{m_j}\,\phi\,(\mathrm{V_j})] \\ & - (1/\mathrm{M_1})\ (1/\mathrm{m_j})\ \alpha^*_{\mathrm{s1}}(\mathrm{l})\,\mathrm{V^*_1}(\ell)\end{aligned}$$

Or

$$\phi\,(E_{\mathrm{Sj}}\mathrm{; def}) = (\mathrm{V^*_1}(\ell)/\mathrm{m_j\,M_1})\ [\alpha_s\mathrm{(aq)} - \alpha^*_{\mathrm{s1}}(\ell)] + \alpha_s\mathrm{(aq)}\,\phi\,(\mathrm{V_j})$$

Or

$$\phi\left(E_{sj};\mathrm{def}\right)=\left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}\,\left[\alpha_\mathrm{s}(\mathrm{aq})-\alpha_{\mathrm{s1}}^*(\ell)\right]+\alpha_\mathrm{s}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$

Also $\left[\mathrm{m_j}\,\rho_1^*(\ell)\right]^{-1}=\left[1/\mathrm{c_j}\right]-\phi\left(\mathrm{V_j}\right)$ Then,

$$\phi\left(\mathrm{E_{sj}};\mathrm{def}\right)=\left[\left(1/\mathrm{c_j}\right)-\phi\left(\mathrm{V_j}\right)\right]\,\left[\alpha_\mathrm{s}(\mathrm{aq})-\alpha_{\mathrm{sl}}^*(\ell)\right]+\alpha_\mathrm{s}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)$$

Or,

$$\begin{aligned}\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right)=\left(1/\mathrm{c_j}\right)\,\left[\alpha_\mathrm{s}(\mathrm{aq})-\alpha_{\mathrm{s1}}^*(\ell)\right]&\\ -\phi\left(\mathrm{V_j}\right)\,\alpha_\mathrm{s}(\mathrm{aq})+\phi\left(\mathrm{V_j}\right)\,\alpha_{\mathrm{s1}}^*(\ell)+\alpha_\mathrm{s}(\mathrm{aq})\,\phi\left(\mathrm{V_j}\right)&\end{aligned}$$

Hence,

$$\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right)=\left(1/\mathrm{c_j}\right)\,\left[\alpha_\mathrm{s}(\mathrm{aq})-\alpha_{\mathrm{S1}}^*(\ell)\right]+\phi\left(\mathrm{V_j}\right)\,\alpha_{\mathrm{s1}}^*(\ell)$$

For further details see----

J.C.R.Reis, G. Douheret, M.I.Davis, I.J.Fjellanger and H.Hoiland, Phys. Chem. Chem. Phys., 2008,10, 561.

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1.12.18: Expansions- Solutions- Isentropic Dependence of Apparent Molar Volume of Solute on Temperature and Pressure

The starting point is the following calculus operation.

$$\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{T}}\right)_{\mathrm{s}}=\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{s}}\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right)_{\mathrm{s}}$$

Also

$$\left(\frac{\partial \phi\left(V_{\mathrm{j}}\right)}{\partial T}\right)_{\mathrm{s}}=\frac{\mathrm{C_p}}{\mathrm{T}}\left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{p}}\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right)_{\mathrm{s}}$$

Or,

$$\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{T}}\right)_{\mathrm{s}}=\frac{\mathrm{C_p}}{\mathrm{T}}\frac{\mathrm{V}}{\mathrm{V}}\left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{p}}\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right)_{\mathrm{s}}$$

Hence,

$$\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial T}\right)_{\mathrm{s}}=\frac{\sigma}{\mathrm{T}\,\alpha_{\mathrm{p}}}\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right)_{\mathrm{s}}$$

But $\frac{\sigma}{\mathrm{T}}=\frac{\left[\alpha_p\right]^2}{\delta}$ Then

$$\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{T}}\right)_{\mathrm{s}}=\frac{\alpha_{\mathrm{p}}}{\delta}\left(\frac{\partial \phi\left(\mathrm{V_j}\right)}{\partial \mathrm{p}}\right)_{\mathrm{s}}$$

Also,

$$\alpha_{\mathrm{s}}=-\kappa_{\mathrm{s}}\,\sigma/\mathrm{T}\,\alpha_{\mathrm{p}}$$

Then $\frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}}=-\frac{\alpha_{\mathrm{p}}}{\delta}$ Hence

$$\frac{\left[\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{T}\right]_{\mathrm{s}}}{\alpha_{\mathrm{s}}}=-\frac{\left[\partial \phi\left(\mathrm{V_j}\right)/\partial \mathrm{p}\right]_{\mathrm{s}}}{\kappa_{\mathrm{s}}}$$

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1.12.19: Expansions- Solutions- Isentropic Dependence of Partial Molar Volume on Temperature

We switch the condition on a derivative expressing the dependence of partial molar volume on temperature.

$$\left(\frac{\partial \mathrm{V_j}}{\partial \mathrm{T}}\right)_{\mathrm{s}} = \left(\frac{\partial \mathrm{V_j}}{\partial \mathrm{T}}\right)_{\mathrm{p}} + \left(\frac{\partial \mathrm{V_j}}{\partial \mathrm{p}}\right)_{\mathrm{T}} \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{s}}$$

Then

$$\left(\frac{\partial V_j}{\partial T}\right)_{\mathrm{s}} = E_{pj} - \left(\frac{\partial V_j}{\partial p}\right)_{T} \frac{(\partial S/\partial T)_p}{(\partial S/\partial p)_T}$$

Or,

$$\left(\frac{\partial \mathrm{V_j}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \mathrm{E_{pj}} + \frac{(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{p}}}{(\partial \mathrm{S}/\partial \mathrm{p})_{\mathrm{T}}} \mathrm{K_{T_j}}$$

But

$$\frac{(\partial S/\partial T)_p}{(\partial S/\partial p)_T} = -\frac{C_p}{T\,(\partial V/\partial T)_p} = -\frac{C_p}{T\,V\,\alpha_p}$$

Or,

$$\frac{(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{p}}}{(\partial \mathrm{S}/\partial \mathrm{p})_{\mathrm{T}}} = -\frac{\sigma}{\mathrm{T}\,\alpha_{\mathrm{p}}}$$

Hence,

$$\left(\frac{\partial \mathrm{V_j}}{\partial \mathrm{T}}\right)_{\mathrm{s}} = \mathrm{E_{pj}} - \frac{\sigma}{\mathrm{T}\,\alpha_{\mathrm{p}}} \mathrm{K_{T_j}}$$

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1.12.20: Expansions- Isentropic- Liquid Mixtures

A given binary liquid mixture has mole fraction $x_1\,[=1-x_2]$ at temperature T and pressure p. The system is at equilibrium at a minimum in Gibbs energy where the affinity for spontaneous change is zero. The molar volume and molar entropy of the mixtures are given by equations (a) and (b).

$$\mathrm{V_m} = \mathrm{V_m}\,[\mathrm{T}, \mathrm{p}, \mathrm{x_1}]$$

$$\mathrm{S_m} = \mathrm{S_m}\,[\mathrm{T}, \mathrm{p}, \mathrm{x_1}]$$

These two equations describe the properties of the system in the $\mathrm{T}-\mathrm{p}$-composition domain; i.e. a Gibbsian description. We consider two dependences of the volume on temperature under the constraint that the affinity for spontaneous change remains at zero; i.e equilibrium expansions.The isobaric expansion is defined by equation (c).

$$\mathrm{E_p(mix)} = \left(\frac{\partial \mathrm{V(mix)}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

The isentropic expansion is defined by equation (d)

$$\mathrm{E_S(mix)} = \left(\frac{\partial \mathrm{V(mix)}}{\partial \mathrm{T}}\right)_{\mathrm{S}}$$

In the latter case the system tracks a path with increase in temperature where the affinity for spontaneous change remains at zero and the entropy remains the same at that defined by equation (b). [NB $\mathrm{E}_p(\mathrm{mix})$ and $E_S(\mathrm{mix})$ as defined by equations (c) and (d) are extensive properties.] The two expansions are related through the (equilibrium) isobaric heat capacity $\mathrm{C_p(mix)}$and the (equilibrium) isothermal compression $\mathrm{K_T(mix)}$ [1]. Thus

$$\mathrm{E_S(mix)} = \mathrm{E_p(mix)} - \frac{\mathrm{C_p(mix)\,K_T(mix)}}{\mathrm{T\,E_p(mix)}}$$

In the context of the property \(\mathrm{E}_{\mathrm{p}(\operatorname{mix})}\), the entropy of the system changes with an increase in temperature at constant pressure. But by definition the entropy does not change for an isentropic expansion, \(\mathrm{E}_{\mathrm{S}(\operatorname{mix})}\).

For a binary liquid mixture having ideal thermodynamic properties,

$$E_S(\mathrm{mix}; id) = E_p(\mathrm{mix}; id) - \frac{C_p(\mathrm{mix}; id)\,K_T(\mathrm{mix}; id)}{T\,E_p(\mathrm{mix}; id)}$$

In this comparison we note that \(\mathrm{E}_{\mathrm{p}(\operatorname{mix})}\) and $\mathrm{E_p(mix;\,id)}$ refer to the same pressure but the entropies referred to in $\mathrm{E_S(mix)}$ and $\mathrm{E_S(mix;\,id)}$ are not the same. The same contrast arises when we set out the two equations describing expansions of the pure liquids.

$$\mathrm{E^*_{S1}}(\ell) = \mathrm{E^*_{p1}}(\ell) - \frac{\mathrm{C^*_{p1}}(\ell)\,\mathrm{K^*_{T1}}(\ell)}{\mathrm{T\,E^*_{p1}}(\ell)}$$

$$\mathrm{E^*_{S2}}(\ell) = \mathrm{E^*_{p2}}(\ell) - \frac{\mathrm{C^*_{p2}}(\ell)\,\mathrm{K^*_{T2}}(\ell)}{\mathrm{T\,E^*_{p2}}(\ell)}$$

The subject is complicated by the galaxy of entropies implied by the phrase ‘at constant entropy’.

Footnote

[1] Using a calculus operation,

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}} - \left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{p}} \left(\frac{\partial \mathrm{p}}{\partial \mathrm{S}}\right)_{\mathrm{T}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

We note two Maxwell equations. From $\mathrm{U} = \mathrm{U[S, V]}, \quad \partial^2\mathrm{U}/\partial\mathrm{S}\,\partial\mathrm{V} = \partial^2\mathrm{U}/\partial\mathrm{V}\,\partial\mathrm{S}$ Then

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{s}} = -\left(\frac{\partial \mathrm{p}}{\partial \mathrm{S}}\right)_{\mathrm{V}}$$

We invert the latter equation. Hence

$$\mathrm{E_S} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_\mathrm{s} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_\mathrm{V} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_\mathrm{s}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_\mathrm{p}$$
$$= -\mathrm{K_S}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_\mathrm{p}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_\mathrm{p} = -\mathrm{K_s}\,\mathrm{C_p}/\mathrm{T}\,\mathrm{E_p}$$

Similarly

$$\partial^2 \mathrm{G}/\partial \mathrm{T}\,\partial \mathrm{p} = \partial^2 \mathrm{G}/\partial \mathrm{p}\,\partial \mathrm{T}$$

Then,

$$E_p = \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

Also at equilibrium, $\mathrm{S} = -\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_\mathrm{p}$

But $\mathrm{G} = \mathrm{H} - \mathrm{T}\,\mathrm{S}$. Then $\mathrm{H} = \mathrm{G} - \mathrm{T}\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_\mathrm{p}$

$$\frac{\partial \mathrm{H}}{\partial \mathrm{T}} = \frac{\partial \mathrm{G}}{\partial \mathrm{T}} - \mathrm{T}\left(\frac{\partial^2 \mathrm{G}}{\partial \mathrm{T}^2}\right) - \frac{\partial \mathrm{G}}{\partial \mathrm{T}}$$

Further,

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_\mathrm{p} = \mathrm{C_p} = -\mathrm{T}\left(\frac{\partial^2 \mathrm{G}}{\partial \mathrm{T}^2}\right)_\mathrm{p} = \mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_\mathrm{p}$$

Based on equation (a), $\mathrm{E_S} = \mathrm{E_p} - \mathrm{C_p}\,\mathrm{K_T}/\mathrm{T}\,\mathrm{E_p}$

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1.12.21: Expansions- Solutions- Partial Molar Isobaric and Isentropic

The starting point is equation (a).

$$\mathrm{E_p} = \mathrm{E_S} + \frac{\mathrm{K_T\,C_p}}{\mathrm{T\,E_p}}$$

We differentiate this equation with respect to the amount of solute n_j at fixed T, p and amount of solvent n_1.

$$\mathrm{E_{pj}} = \mathrm{E_{Sj}} + \frac{1}{\mathrm{T}}\left[\frac{\mathrm{K_T}}{\mathrm{E_p}}\,\mathrm{C_{pj}} + \frac{\mathrm{C_p}}{\mathrm{E_p}}\,\mathrm{K_{Tj}} - \frac{\mathrm{K_T\,C_p}}{(\mathrm{E_p})^2}\,\mathrm{E_{pj}}\right]$$

Or,

$$\mathrm{E_{pj}} = \mathrm{E_{Sj}} + \frac{1}{\mathrm{T}}\,\frac{\mathrm{K_T\,C_p}}{\mathrm{E_p}}\left[\frac{\mathrm{C}_{pj}}{\mathrm{C_p}} + \frac{\mathrm{K_{TJ}}}{\mathrm{K_T}} - \frac{\mathrm{E}_{pj}}{\mathrm{E_p}}\right]$$

We convert to volume intensive variables.

$$\mathrm{E_{pj}} = \mathrm{E_{Sj}} + \frac{1}{\mathrm{T}}\,\frac{\kappa_\mathrm{T}\,\mathrm{C_p}}{\alpha_\mathrm{p}\,\mathrm{V}}\left[\frac{\mathrm{V\,C_{pj}}}{\mathrm{C_p}} + \frac{\mathrm{V\,K}_{Tj}}{\mathrm{K_T}} - \frac{\mathrm{V\,E_{pj}}}{\mathrm{E_p}}\right]$$

Or,

$$E_{pj} = E_{Sj} + \frac{1}{T}\,\frac{K_T\,\sigma}{\alpha_p}\left[\frac{C_{pj}}{\sigma} + \frac{K_{T_j}}{K_T} - \frac{E_{pj}}{\alpha_p}\right]$$

But

$$\varepsilon = K_\mathrm{T}\,\sigma/\mathrm{T}\,\alpha_\mathrm{p}$$

Then,

$$\frac{\mathrm{E_{pj}} - \mathrm{E}_{Sj}}{\varepsilon} = -\frac{\mathrm{E_{pj}}}{\alpha_\mathrm{p}} + \frac{\mathrm{K}_{Tj}}{\kappa_\mathrm{T}} + \frac{\mathrm{C_{pj}}}{\sigma}$$

Hence for an aqueous solution in the limit of infinite dilution,

$$\frac{\mathrm{E^\infty_{pj}(aq)} - \mathrm{E^\infty_{sj}(aq)}}{\varepsilon^*_1(\ell)} = -\frac{\mathrm{E^\infty_{pj}(aq)}}{\alpha^*_{\mathrm{p}1}(\ell)} + \frac{\mathrm{K^\infty_{T}}_j\mathrm{(aq)}}{\kappa^*_{\mathrm{T}1}(\ell)} + \frac{\mathrm{C^\infty_{pj}}}{\sigma^*_1(\ell)}$$

We start with the equation,

$$\mathrm{E_s} = -\frac{\mathrm{K_s\,C_p}}{\mathrm{T\,E_p}}$$

The latter equation is differentiated with respect to the amount of solute n_j in a solution at fixed T, fixed p and fixed amount of solvent, n_1.

$$\left(\frac{\partial E_S}{\partial n_j}\right)_{T,p,n(1)} = -\frac{C_p}{T\,E_p}\left(\frac{\partial K_s}{\partial n_j}\right)_{T,p,n(1)} - \frac{K_s}{T\,E_p}\left(\frac{\partial C_p}{\partial n_j}\right)_{T,p,n(1)} + \frac{K_s\,C_p}{T\,(E_p)^2}\left(\frac{\partial E_p}{\partial n_j}\right)_{T,p,n(1)}$$

Or,

$$E_{S_j} = -\frac{C_p}{T\,E_p}\,\frac{K_s}{K_s}\,K_{s_j} - \frac{K_s}{T\,E_p}\,\frac{C_p}{C_p}\,C_{pj} + \frac{K_s\,C_p}{T\,(E_p)^2}\,E_{pj}$$

We rewrite the latter equation in terms of volume intensive variables.

$$\mathrm{E_{Sj}} = -\frac{1}{\mathrm{T}}\,\frac{\sigma}{\alpha_\mathrm{p}}\,\frac{\kappa_\mathrm{s}}{\kappa_\mathrm{s}}\,\mathrm{K_{Sj}} - \frac{1}{\mathrm{T}}\,\frac{\kappa_\mathrm{S}}{\alpha_\mathrm{p}}\,\frac{\sigma}{\sigma}\,\mathrm{C_{pj}} + \frac{\kappa_\mathrm{s}\,\sigma}{\mathrm{T}\,(\alpha_\mathrm{p})^2}\,\mathrm{E_{pj}}$$

But

$$\alpha_{\mathrm{s}} = -\frac{\kappa_{\mathrm{s}}\,\sigma}{\mathrm{T}\,\alpha_{\mathrm{p}}}$$

Then

$$E_{\mathrm{S_j}} = \alpha_{\mathrm{s}}\,\frac{\mathrm{K_{sj}}}{\kappa_{\mathrm{s}}} + \alpha_{\mathrm{s}}\,\frac{\mathrm{C}_{pj}}{\sigma} - \alpha_{\mathrm{s}}\,\frac{\mathrm{E_{pj}}}{\alpha_{\mathrm{p}}}$$

Therefore (with a change of order)

$$\frac{E_{sj}}{\alpha_p} = -\frac{E_{pj}}{\alpha_p} + \frac{K_{Sj}}{K_s} + \frac{C_{pj}}{\sigma}$$

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1.12.22: Expansions and Compressions- Solutions- Isentropic Dependence of Volume on Temperature and Pressure

The starting point is the calculus operation for a double differential.

$$\frac{\partial^2 U}{\partial S\,\partial V} = \frac{\partial^2 U}{\partial V\,\partial S}$$

Then, $\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial p}{\partial S}\right)_v$ Or,

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{s}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{V}}$$

But,

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{s}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{s}} \left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{p}}$$

Also we note that

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{p}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

Then,

$$\left(\frac{\partial V}{\partial T}\right)_s = \left(\frac{\partial V}{\partial p}\right)_s \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p$$

However from the Gibbs - Helmholtz Equation, $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$

Then $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{s}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{s}} \left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{p}} \frac{\mathrm{C_p}}{\mathrm{T}}$ Or,

$$\mathrm{E_s} = -\frac{\mathrm{K_s\,C_p}}{\mathrm{T\,E_p}}$$

We divide both sides of equation (f) by volume V. Hence

$$\alpha_{\mathrm{s}} = -\kappa_{\mathrm{s}}\,\sigma/\mathrm{T}\,\alpha_{\mathrm{p}}$$

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1.12.23: Expansions- The Difference

For a solution,

$$\varepsilon = \alpha_p - \alpha_s = \kappa_T \, \sigma / T \, \alpha_p$$

In order to simplify the algebra, we omit (aq) and (ℓ) when describing the properties of an aqueous solution and the pure liquid respectively. Superscript '*' identifies the pure solvent.

$$\varepsilon^* = \alpha_{\mathrm{p}}^* - \alpha_{\mathrm{S}}^* = \kappa_{\mathrm{T}}^* \, \sigma^* / \mathrm{T} \, \alpha_{\mathrm{p}}^*$$

Hence,

$$\varepsilon - \varepsilon^* = \frac{\varepsilon}{\kappa_{\mathrm{T}} \, \sigma} \left[\kappa_{\mathrm{T}} \, \sigma - \kappa_{\mathrm{T}}^* \, \sigma^*\right] - \frac{\varepsilon^*}{\alpha_{\mathrm{p}}} \left[\alpha_{\mathrm{p}} - \alpha_{\mathrm{p}}^*\right]$$

The latter equation is effectively an identity. According to equation (c)

$$\varepsilon - \varepsilon = \varepsilon - \frac{\varepsilon}{\kappa_{\mathrm{T}} \, \sigma} \, \kappa_{\mathrm{T}}^* \, \sigma^* - \varepsilon + \frac{\varepsilon}{\alpha_{\mathrm{p}}} \, \alpha_{\mathrm{p}}^*$$

We use equations (a) and (b) in the second and fourth terms on the right hand side of the latter equation.

$$\varepsilon - \varepsilon^* = \varepsilon - \frac{\varepsilon}{\kappa_{\mathrm{T}} \, \sigma} \, \varepsilon^* \, \mathrm{T} \, \alpha_{\mathrm{p}}^* - \varepsilon^* + \frac{\varepsilon^* \, \alpha_{\mathrm{p}}^* \, \mathrm{T} \, \varepsilon}{\kappa_{\mathrm{T}} \, \sigma}$$

Or $\varepsilon - \varepsilon^* = \varepsilon - \varepsilon^*$ Further, as an identity,

$$\kappa_{\mathrm{T}} \, \sigma - \kappa_{\mathrm{T}}^* \, \sigma^* = \sigma \, \left(\kappa_{\mathrm{T}} - \kappa_{\mathrm{T}}^*\right) + \kappa_{\mathrm{T}}^* \, \left(\sigma - \sigma^*\right)$$

From equation (c),

$$\varepsilon - \varepsilon^* = \frac{\varepsilon}{\kappa_{\mathrm{T}}} \left[\kappa_{\mathrm{T}} - \kappa_{\mathrm{T}}^*\right] + \frac{\varepsilon \, \kappa_{\mathrm{T}}^*}{\kappa_{\mathrm{T}} \, \sigma} \left(\sigma - \sigma^*\right) - \frac{\varepsilon^*}{\alpha_{\mathrm{p}}} \left[\alpha_{\mathrm{p}} - \alpha_{\mathrm{p}}^*\right]$$

But

$$\phi\left(\mathrm{E_{sj}}; \mathrm{def}\right) = \frac{\alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^*}{\mathrm{c_j}} + \alpha_{\mathrm{s}}^* \, \phi\left(\mathrm{V_j}\right)$$

The analogue for $\phi\left(E_{pj}\right)$ is the following equation. $\phi\left(\mathrm{E_{pj}}\right) = \frac{\alpha_{\mathrm{p}} - \alpha_{\mathrm{p}}^*}{\mathrm{c_j}} + \alpha_{\mathrm{p}}^* \, \phi\left(\mathrm{V_j}\right)$ Hence

$$\phi\left(E_{pj}\right) - \phi\left(E_{S_j}; \mathrm{def}\right) = \frac{\varepsilon - \varepsilon^*}{c_j} + \varepsilon^* \, \phi\left(V_j\right)$$

From equation (g), dividing by c_j,

$$\frac{\varepsilon - \varepsilon}{c_j} = \frac{\varepsilon}{\kappa_T} \frac{1}{c_j} \left[\kappa_T - \kappa_T^*\right] + \frac{\varepsilon \, \kappa_T^*}{\kappa_T \, \sigma} \frac{1}{c_j} \left[\sigma - \sigma^*\right] - \frac{\varepsilon^*}{\alpha_p} \frac{1}{c_j} \left[\alpha_p - \alpha_p^*\right]$$

But from equation (i)

$$\frac{\varepsilon - \varepsilon^*}{c_j} = \phi\left(E_{pj}\right) - \phi\left(E_{Sj}; \mathrm{def}\right) - \varepsilon^* \, \phi\left(V_j\right)$$

Equations having similar form for $\left(\kappa_{\mathrm{T}} - \kappa_{\mathrm{T}}^*\right), \left(\sigma - \sigma^*\right)$ and $\left(\alpha_p - \alpha_p^*\right)$ are readily generated. Hence

$$\phi\left(\mathrm{E_{pj}}\right) - \phi\left(\mathrm{E_{Sj}}; \mathrm{def}\right) = \frac{\varepsilon}{\kappa_{\mathrm{T}}} \left[\phi\left(\mathrm{K_{Tj}}\right) - \kappa_{\mathrm{T}}^* \, \phi\left(\mathrm{V_j}\right)\right] + \frac{\varepsilon \, \kappa_{\mathrm{T}}^*}{\kappa_{\mathrm{T}} \, \sigma} \left[\phi\left(\mathrm{C_{pj}}\right) - \sigma^* \, \phi\left(\mathrm{V_j}\right)\right] - \frac{\varepsilon^*}{\alpha_{\mathrm{p}}} \left[\phi\left(\mathrm{E_{pj}}\right) - \alpha_{\mathrm{p}}^* \, \phi\left(\mathrm{V_j}\right)\right] + \varepsilon^* \, \phi\left(\mathrm{V_j}\right)$$

Therefore

$$\phi\left(E_{\mathrm{pj}}\right)-\phi\left(E_{\mathrm{Sj}};\mathrm{def}\right)=-\frac{\varepsilon}{\alpha_{\mathrm{p}}}\,\phi\left(\mathrm{E_{pj}}\right)+\frac{\varepsilon}{\kappa_{\mathrm{T}}}\,\phi\left(\mathrm{K_{Tj}}\right)+\frac{\varepsilon\,\kappa_{\mathrm{T}}^{*}}{\kappa_{\mathrm{T}}\,\sigma}\,\phi\left(\mathrm{C_{pj}}\right)$$
$$+\left[\varepsilon*\left(1+\frac{\alpha_{\mathrm{p}}^{*}}{\alpha_{\mathrm{p}}}\right)-\frac{\varepsilon\,\kappa_{\mathrm{T}}^{*}}{\kappa_{\mathrm{T}}}\,\left(1+\frac{\sigma^{*}}{\sigma}\right)\right]\,\phi\left(\mathrm{V_{j}}\right)\quad(\mathrm{m})$$

In the limit of infinite dilution,

$$\frac{\phi\left(E_{\mathrm{pj}}\right)^{\infty}-\phi\left(\mathrm{E_{Sj}};\mathrm{def}\right)^{\infty}}{\varepsilon_{1}^{*}(\ell)}=-\frac{\phi\left(\mathrm{E_{pj}}\right)^{\infty}}{\alpha_{\mathrm{p1}}^{*}(\ell)}+\frac{\phi\left(\mathrm{K_{T}}\right)^{\infty}}{\kappa_{\mathrm{Tl}}^{*}(\ell)}+\frac{\phi\left(\mathrm{C_{pj}}\right)^{\infty}}{\sigma_{1}^{*}(\ell)}$$

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1.12.24: Expansions- Equations

We simplify the algebra by omitting the descriptors (aq) and (ℓ) in the following equations. The starting point is the following equation.

$$\alpha_S - \alpha_S^* = \frac{\alpha_S}{\kappa_S\,\sigma}\,(\kappa_S\,\sigma - \kappa_S^*\,\sigma^*) - \frac{\alpha_S^*}{\alpha_p}\,(\alpha_p - \alpha_p^*)$$

The latter equation is effectively an identity. Thus from equation (a)

$$\alpha_S - \alpha_S^* = \alpha_S - \frac{\alpha_S}{\kappa_S\,\sigma}\,\kappa_S^*\,\sigma^* - \alpha_S^* + \frac{\alpha_S^*}{\alpha_p}\,\alpha_p^*$$

But $\alpha_{\mathrm{s}} = -\kappa_{\mathrm{s}}\,\sigma/\mathrm{T}\,\alpha_{\mathrm{p}}$ and $\alpha_{\mathrm{p}}^*/\alpha_{\mathrm{s}}^* = -\kappa_{\mathrm{s}}^*\,\sigma^*/\mathrm{T}$

Then from (b), $\alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^* = \alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^* + \frac{\kappa_{\mathrm{s}}\,\sigma}{\mathrm{T}\,\alpha_{\mathrm{p}}\,\kappa_{\mathrm{s}}\,\sigma}\,\kappa_{\mathrm{s}}^*\,\sigma^* - \frac{\kappa_{\mathrm{s}}^*\,\sigma^*}{\alpha_{\mathrm{p}}\,\mathrm{T}}$ or $\alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^* = \alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^*$

But as an identity,

$$\kappa_{\mathrm{S}}\,\sigma - \kappa_{\mathrm{S}}^*\,\sigma^* = \sigma\,(\kappa_{\mathrm{S}} - \kappa_{\mathrm{S}}^*) + \kappa_{\mathrm{S}}^*\,(\sigma - \sigma^*)$$

Then from equations (a) and (c),

$$\alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^* = \frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}}\,(\kappa_{\mathrm{s}} - \kappa_{\mathrm{s}}^*) + \frac{\alpha_{\mathrm{s}}\,\kappa_{\mathrm{s}}^*}{\kappa_{\mathrm{s}}\,\sigma}\,(\sigma - \sigma^*) - \frac{\alpha_{\mathrm{s}}^*}{\alpha_{\mathrm{p}}}\,(\alpha_{\mathrm{p}} - \alpha_{\mathrm{p}}^*)$$

But,

$$\phi\,(E_{\mathrm{S}};\mathrm{def}) = [\mathrm{c_j}]^{-1}\,(\alpha_{\mathrm{s}} - \alpha_{\mathrm{s}}^*) + \alpha_{\mathrm{s}}^*\,\phi\,(\mathrm{V_j})$$

Hence

$$\begin{aligned}\phi\,(E_{\mathrm{s}j};\mathrm{def}) =& \frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}}\,[\mathrm{c_j}]^{-1}\,(\kappa_{\mathrm{s}} - \kappa_{\mathrm{s}}^*) + \frac{\alpha_{\mathrm{s}}\,\kappa_{\mathrm{s}}^*}{\kappa_{\mathrm{s}}\,\sigma}\,[\mathrm{c_j}]^{-1}\,(\sigma - \sigma^*)\\ &- \frac{\alpha_{\mathrm{s}}^*}{\alpha_{\mathrm{p}}}\,[\mathrm{c_j}]^{-1}\,(\alpha_{\mathrm{p}} - \alpha_{\mathrm{p}}^*) + \alpha_{\mathrm{s}}^*\,\phi\,(\mathrm{V_j})\end{aligned}$$

For isobaric heat capacities,

$$\phi\,(\mathrm{C_{pj}}) = [\mathrm{c_j}]^{-1}\,(\sigma - \sigma^*) + \sigma^*\,\phi\,(\mathrm{V_j})$$

Also

$$\phi\,(K_{\mathrm{S}_j};\mathrm{def}) = [\mathrm{c_j}]^{-1}\,(\kappa_{\mathrm{s}} - \kappa_{\mathrm{s}}^*) + \kappa_{\mathrm{s}}^*\,\phi\,(\mathrm{V_j})$$

Hence

$$\begin{aligned}\phi\,(\mathrm{E}_{sj};\mathrm{def}) =& \frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}}\,[\phi\,(\mathrm{K}_{sj};\mathrm{def}) - \kappa_{\mathrm{s}}^*\,\phi\,(\mathrm{V_j})] + \frac{\alpha_{\mathrm{s}}\,\kappa_{\mathrm{s}}^*}{\kappa_{\mathrm{s}}\,\sigma}\,[\phi\,(\mathrm{C_{pj}}) - \sigma^*\,\phi\,(\mathrm{V_j})]\\ &- \frac{\alpha_{\mathrm{s}}^*}{\alpha_{\mathrm{p}}}\,[\phi\,(\mathrm{E_{pj}}) - \alpha_{\mathrm{p}}^*\,\phi\,(\mathrm{V_j})] + \alpha_{\mathrm{s}}^*\,\phi\,(\mathrm{V_j})\end{aligned}$$

Then with a little reorganisation,

$$\begin{aligned}\phi\,(\mathrm{E}_{sj};\mathrm{def}) =& -\frac{\alpha_{\mathrm{s}}^*}{\alpha_{\mathrm{p}}}\,\phi\,(\mathrm{E_{p}}j) + \frac{\alpha_{\mathrm{s}}}{\kappa_{\mathrm{s}}}\,\phi\,(\mathrm{K}_{sj};\mathrm{def}) + \frac{\alpha_{\mathrm{s}}\,\kappa_{\mathrm{s}}^*}{\kappa_{\mathrm{s}}\,\sigma}\,\phi\,(\mathrm{C_{pj}})\\ &+ \left[\alpha_{\mathrm{s}}^*\left(1 + \frac{\alpha_{\mathrm{p}}^*}{\alpha_{\mathrm{p}}}\right) - \frac{\alpha_{\mathrm{s}}\,\kappa_{\mathrm{s}}^*}{\kappa_{\mathrm{s}}}\left(1 + \frac{\sigma^*}{\sigma}\right)\right]\phi\,(\mathrm{V_j})\end{aligned}$$

Hence, in the limit of infinite dilution, $\frac{\phi(\mathrm{E_{Sj}};\mathrm{def})^\infty}{\alpha_{\mathrm{S1}}^*(\ell)} = -\frac{\phi(\mathrm{E_{pj}})^\infty}{\alpha_{\mathrm{p1}}^*(\ell)} + \frac{\phi(\mathrm{K}_{sj};\mathrm{def})^\infty}{\kappa_{\mathrm{s1}}^*(\ell)} + \frac{\phi(\mathrm{C_{pj}})^\infty}{\sigma_1^*(\ell)}$

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1.13: Equilibrium

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1.13.1: Equilibrium and Frozen Properties

The Gibbs energy G of a given closed system is characterised by the independent variables temperature T, pressure p and composition ξ.

$$\mathrm{G} = \mathrm{G}[\mathrm{T}, \mathrm{p}, \xi] \tag{1.13.1.1}$$

In the state defined by Equation 1.13.1.1 the affinity for spontaneous change is A. Starting with the system in the state defined by equation (a) it is possible to change the pressure (at fixed temperature) and thereby perturb the system to neighbouring states where the affinity A is the same. The differential dependence of G on pressure along this path is given by the partial differential $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T,A}}$. Returning to the state defined by Equation 1.13.1.1 we envisage a perturbation by a change in pressure (at fixed temperature) along a path such that the extent of chemical reaction ξ remains constant; the corresponding differential dependence of G is given by $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T},\xi}$.The two partial derivatives are related by equation (b) for a system at constant temperature.

$$\left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\mathrm{A}} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\xi} - \left[\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right]_{\xi} \left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{p}} \left[\frac{\partial \mathrm{G}}{\partial \xi}\right]_{\mathrm{p}} \tag{1.13.1.2}$$

The important result which emerges from this equation concerns the properties of a system at chemical equilibrium where the affinity for spontaneous change is zero, the rate of change $\mathrm{d}\xi/\mathrm{dt}$ is zero, the Gibbs energy is a minimum and, significantly, $(\partial G/\partial \xi)_{\mathrm{T,p}}$ is zero. Hence

$$V = \left[\frac{\partial G}{\partial p}\right]_{T,A=0} = \left[\frac{\partial G}{\partial p}\right]_{T,\xi(eq)}$$

Thus we confirm that the volume V of a system is a strong state variable, the dependence of G on pressure (at constant T) at constant '$\mathrm{A} = 0$' and at constant composition, ξ^{eq} are identical. However if we turn our attention on to expansibilities and compressibilities we find that it is important to distinguish between two sets of properties, equilibrium and frozen.

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1.13.2: Equilibrium- Isochoric and Isobaric Paramenters

In a description of a given closed system we define two extensive state variables, the Gibbs energy G and the Helmholtz energy F.

$$\mathrm{G} = \mathrm{U} + \mathrm{p}\,\mathrm{V} - \mathrm{T}\,\mathrm{S}$$

$$\mathrm{F} = \mathrm{U} - \mathrm{T}\,\mathrm{S}$$

Hence,

$$\mathrm{G} = \mathrm{F} + \mathrm{p}\,\mathrm{V}$$

The latter interesting equation links two practical thermodynamic potentials;

i. G for processes at fixed T and p,
ii. F for processes at fixed T and V.

The dependence of G on extent of reaction at constant temperature and pressure is related to the differential dependence of F on ξ at fixed temperature and pressure.

$$\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{\mathrm{T,p}} = \left(\frac{\partial \mathrm{F}}{\partial \xi}\right)_{\mathrm{T,p}} + \mathrm{p}\left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}}$$

At equilibrium where $\mathrm{A} = 0$, \(\xi = \xi^{\mathrm{eq}}\) and the Gibbs energy is a minimum [i.e. $(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}} = 0$],

$$\left(\frac{\partial F}{\partial \xi}\right)_{\mathrm{T,p,A=0}} = \mathrm{p}\left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p,A=0}}$$

In other words the differential dependence of the Helmholtz energy on extent of reaction at equilibrium (at constant T and p) is related to the volume of reaction. We rewrite equation (c);

$$\mathrm{F} = \mathrm{G} - \mathrm{p}\,\mathrm{V}$$

At constant temperature and volume,

$$\left(\frac{\partial \mathrm{F}}{\partial \xi}\right)_{\mathrm{T,V}} = \left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{\mathrm{T,V}} - \mathrm{V}\left(\frac{\partial \mathrm{p}}{\partial \xi}\right)_{\mathrm{T,V}}$$

At equilibrium (at constant T and V) where the Helmholtz energy F is a minimum, clearly the Gibbs energy is not at a minimum. The dependence of both G and F on temperature at equilibrium can be expressed using two Gibbs - Helmholtz equations. Thus,

$$\left[\frac{\partial(\Delta \mathrm{G}/\mathrm{T})}{\partial(1/\mathrm{T})}\right]^{\mathrm{eq}}_{\mathrm{p,A=0}} = \Delta \mathrm{H}^{\mathrm{eq}}$$

$$\left[\frac{\partial(\Delta \mathrm{F}/\mathrm{T})}{\partial(1/\mathrm{T})}\right]^{\mathrm{eq}}_{\mathrm{V,A=0}} = \Delta \mathrm{U}^{\mathrm{eq}}$$

From a practical standpoint, determination of $\Delta \mathrm{H}^{\mathrm{eq}}$ is reasonably straightforward because over a range of temperatures the isobaric condition is readily satisfied. Thus we probe this differential dependence at a series of defined temperatures at fixed pressure; i.e. over the range $\mathrm{T} - \delta \mathrm{T}$ to $\mathrm{T} + \delta \mathrm{T}$ about T for a number of temperatures.

The condition ‘at constant volume’ presents problems. In principle we change the pressure to hold V constant over a range of temperatures. Then we probe the differential dependence of $(\Delta \mathrm{F}/\mathrm{T})$ at a series of fixed temperatures; e.g. over the range $\mathrm{T} - \Delta \mathrm{T}$ to $\mathrm{T} - \Delta \mathrm{T}$ about a given temperature T. If the range of temperatures is large, there is a high probability that very high pressures will be required to hold the global isochoric condition.

Another approach probes the dependence of $(\Delta \mathrm{F}/\mathrm{T})$ on temperature at a series of temperatures where volume V is held constant by changing the pressure over the range

\[\mathrm{T}_{\mathrm{i}}-\delta \mathrm{T}\) to

$$\mathrm{T_i} - \delta \mathrm{T}$$

about T_i. Volume V_i is constant over a small range of temperature. Here the isochoric condition is local to temperature T; thus ΔU is obtained at T_i and V_i. Under these circumstances, comparison of derived ΔU - quantities as a function of temperature is not straightforward.

Interestingly the solvent water presents pairs of temperatures either side of the TMD where molar volume of water is the same at, for example, ambient pressure. It might be possible to explore this feature by assuming that the volumes of two very dilute solutions are also identical at matched pairs of temperatures.

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1.13.3: Equilibirium- Solid-Liquid

A given homogeneous liquid system comprises two chemical substances i and j at known T and p. The temperature and/or pressure are changed. Consequently chemical substance j spontaneously separates out as a solid phase but substance i does not. Hence the liquid becomes richer in chemical substance i.

The starting point of the analysis is the following equation for the affinity for spontaneous transfer of substance j from phase II to phase I [1].

$$\delta\left(\frac{A_j}{T}\right) = \frac{\left[\Delta_{\text{trans}}\, H_j^0(T,p)\right]}{T^2}\,\delta T - \frac{\left[\Delta_{\text{trans}}\, V_j^0(T,p)\right]}{T}\,\delta p + R\,\delta \ln\left[\frac{x_j(I)\, f_j(I)}{x_j(\text{ II })\, f_j(II)}\right]$$

For two equilibrium states such that $\delta\,(\mathrm{A_j/T})$ is zero for the transfer of chemical substance j from phase II to phase I,

$$\mathrm{R\,\delta \ln\left[\frac{x_j(II)\, f_j(II)}{x_j(I)\, f_j(I)}\right] = \frac{\left[\Delta_{trans}\, H_j^0(\,T,p)\right]}{T^2}\,\delta T - \frac{\left[\Delta_{trans}\, V_j^0(\,T,p)\right]}{T}\,\delta p}$$

In this application, chemical substance i cannot exist in phase I. Then the equilibrium states are determined by substance j. Further we consider the case where state I corresponds to pure j such that $x_j(I)\, f_j(I)$ is unity at reference temperature $\mathrm{T_{ref}}$ and reference pressure pref. We integrate equation (b) between these two states.

$$\mathrm{\ln\left[x_j(II)\, f_j(II)\right] = \int_{T(ref)}^{T} \frac{\left[\Delta_{trans}\, H_j^0(\,T,p)\right]}{R\,T^2}\,dT - \int_{p(ref)}^{p} \frac{\left[\Delta_{trans}\, V_j^0(\,T,p)\right]}{R\,T}\,dp}$$

In the event that the pressure is constant,

$$\mathrm{\ln\left[x_j(II)\, f_j(II)\right] = \int_{T(ref)}^{T} \frac{\left[\Delta_{trans}\, H_j^0(\,T,p)\right]}{R\,T^2}\,dT}$$

Footnote

[1] By definition, for the transfer of one mole of chemical substance j from phase II to phase I, $A_j = -\left[\mu_j(\mathrm{I}) - \mu_j(\mathrm{II})\right]$; Or, $\mathrm{A_j = \mu_j(II) - \mu_j(I)}$

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1.13.4: Equilibrium- Liquid-Solid- Schroeder - van Laar Equation

A given homogeneous binary liquid system (at pressure p) contains two chemical substances i and j at temperature T. The liquid system is cooled and only substance j separates out as the pure solid substance j. Hence,

$$\ln\left[\mathrm{x_j}(\ell)\,\mathrm{f_j}(\ell)\right] = \int_{\mathrm{T_j^0}}^{\mathrm{T}} \frac{\left[\Delta_{\mathrm{trans}}\,\mathrm{H_j^0}(\,\mathrm{T},\mathrm{p})\right]}{\mathrm{R}\,\mathrm{T}^2}\,\mathrm{dT} \tag{1.13.4.1}$$

Here $x_j(\ell)$ is the mole fraction composition of the liquid; $f_j(\ell)$ is the **rational activity coefficient** of substance j in the liquid mixture at mole fraction $x_j(\ell)$ and temperature T. $\mathrm{T_j^0}$ is the melting point of pure j substance j at pressure p; i.e., both liquid and solid phases are pure chemical substance j.

In the event that $\Delta_{\mathrm{trans}}\,\mathrm{H_j^0}(\,\mathrm{T},\mathrm{p})$ is independent of temperature [i.e. $\Delta_{\mathrm{trans}}\,C_{pj}^0(T,p)$ is zero] Equation 1.13.4.1 is integrated to yield Equation 1.13.4.2.

$$-\ln\left[\mathrm{x_j}(\ell)\,\mathrm{f_j}(\ell)\right] = \frac{\Delta_{\mathrm{fus}}\mathrm{H_j^0}(\,\mathrm{T},\mathrm{p})}{\mathrm{R}}\left(\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T_j^0}}\right) \tag{1.13.4.2}$$

The phenomenon under consideration is fusion so that $\Delta_{\mathrm{fus}}\,\mathrm{H_j^0}(\,\mathrm{T},\mathrm{p})$ is the enthalpy of fusion of chemical substance j at temperature T and pressure p. In the event that the thermodynamic properties of the liquid-solid system are ideal, Equation 1.13.4.2 simplifies to Equation 1.13.4.3.

$$-\ln\left[\mathrm{x_j}(\ell)\right] = \frac{\Delta_{\mathrm{f}}\mathrm{H_j^0}(\,\mathrm{T},\mathrm{p})}{\mathrm{R}}\left(\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T_j^0}}\right) \tag{1.13.4.3}$$

Equation 1.13.4.3 is the Schroeder- van Laar Equation [1].

Footnote

[1] I. Prigogine and R Defay, Chemical Thermodynamics, transl. D. H. Everett, Longmans Greeen, London, 1953.

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1.13.5: Equilibrium - Eutectics

A given homogeneous binary liquid system (at pressure p) contains two chemical substances i and j at temperature T. The liquid system is cooled and only substance j separates out as the pure solid substance j leaving the liquid richer in chemical substance i. The mole fraction composition of the liquid is given by the Schroeder-van Laar equation written in the following form.

$$-\ln\left[\mathrm{x_j}(\ell)\mathrm{f_j}(\ell)\right] = \frac{\left[\Delta_{\mathrm{fus}}\,\mathrm{H_j^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T^0_{fus;\,j}}}\right] \tag{1.13.5.1}$$

In many cases as the mole fraction composition of substance i in the liquid increases the equilibrium temperature T decreases until at the eutectic temperature $\mathrm{T_e}$ and mole fraction $(\mathbf{X_j})_e$ the system comprises a solid, the eutectic mixture. In the event that the thermodynamic properties of the system can be described as ideal, Equation 1.13.5.1 simplifies to Equation 1.13.5.2 where it is assumed that $\mathrm{f_j}(\ell)$ is unity at all temperatures. Then

$$-\ln\left[\mathrm{x_j}(\ell)\right] = \frac{\left[\Delta_{\mathrm{fus}}\mathrm{H_j^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T^0_{fus;\,j}}}\right] \tag{1.13.5.2}$$

For the other component i, a corresponding plot is obtained when on cooling the liquid mixture only pure solid i separates out.

$$-\ln\left[\mathrm{x_i}(\ell)\mathrm{f_i}(\ell)\right] = \frac{\left[\Delta_{\mathrm{fus}}\mathrm{H_i^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T^0_{fus\,;i}}}\right]$$

If the thermodynamic properties of the system are ideal then the analogue of equation (b) is equation (d).

$$-\ln\left[\mathrm{x_i}(\ell)\right] = \frac{\left[\Delta_{\mathrm{fus}}\,\mathrm{H_i^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T^0_{fuss\,;i}}}\right]$$

The two curves described by equations (a) and (c) meet at the eutectic temperature. $\mathrm{T_e}$. Granted that the thermodynamic properties of the system are ideal, the following two equations follow from equations (b) and (d).

$$-\ln\left[\mathrm{x_j^e}(\ell)\right] = \frac{\left[\Delta_{\mathrm{fus}}\mathrm{H_j^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T_e}} - \frac{1}{\mathrm{T^0_{fus\,;j}}}\right]$$

$$-\ln\left[\mathrm{x_i^e}(\ell)\right] = -\ln\left[1-\mathrm{x_j^e}\right] = \frac{\left[\Delta_{\mathrm{fus}}\,\mathrm{H_i^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T_e}} - \frac{1}{\mathrm{T^0_{fuss;\,i}}}\right]$$

In the event that

$$\frac{\left[\Delta_{\mathrm{fus}}\,\mathrm{H_j^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T_e}} - \frac{1}{\mathrm{T^0_{fuss\,;j}}}\right] = \frac{\left[\Delta_{\mathrm{fus}}\,\mathrm{H_i^0}(\,\mathrm{T})\right]}{\mathrm{R}}\left[\frac{1}{\mathrm{T_e}} - \frac{1}{\mathrm{T^0_{fuss\,;i}}}\right]$$

then $x_i^e = x_j^e = 0.5$. The impact of the non-ideal thermodynamic properties can be explored using equation (a) and (c) in conjunction with empirical equations relating, for example, $\mathrm{f_j}(\ell)$ and $\mathrm{x_j}(\ell)$; e.g. equation (g).

$$\ln\left[\mathrm{f_j}(\ell)\right] = \alpha\left[1-\mathrm{x_j}(\ell)\right]^2$$

[1] I. Prigogine and R. Defay, Chemical Thermodynamics, tranls. D. H. Everett, Longmans Greeen, London, 1953.

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1.13.6: Equilibrium - Depression of Freezing Point of a Solvent by a Solute

A given homogeneous liquid system (at pressure p) comprises solvent i and solute j at temperature T and pressure p. In the absence of solute j, the freezing point of the solvent is T_1^0. But in the presence of solute j the freezing point is temperature T where $\mathrm{T} < \mathrm{T}_1^0$. The depression of freezing point $\theta\,[= \mathrm{T}_1^0 - \mathrm{T}]$ is recorded for a solution where the mole fraction of solvent is $\mathrm{x}_1(\mathrm{sln})$. If the solution is dilute, we can assume that the thermodynamic properties of the solution are ideal. From the Schroeder-van Laar equation,

$$-\ln\left[x_1(s\,\mathrm{ln})\right] = \frac{\left[\Delta_f H_1^0(T)\right]}{R}\left[\frac{1}{T} - \frac{1}{T_1^0}\right]$$

$$-\ln\left[\mathrm{x}_1(\ \mathrm{s\,ln})\right] = \frac{\Delta_\mathrm{f}\mathrm{H}_1^0}{\mathrm{R}}\,\frac{\theta}{\left(\mathrm{T}_1^0 - \theta\right)\,\mathrm{T}_1^0}$$

If

$$\mathrm{T}_1^0 - \theta \cong \mathrm{T}_1^0, -\ln\left[\mathrm{x}_1(\ \mathrm{s\,ln})\right] = \frac{\Delta_\mathrm{f}\mathrm{H}_1^0}{\mathrm{R}}\,\frac{\theta}{\left(\mathrm{T}_1^0\right)^2}$$

Or,

$$\ln\left[\frac{1}{x_1(s\,\mathrm{ln})}\right] = \frac{\Delta_\mathrm{f}H_1^0}{R}\,\frac{\theta}{\left(T_1^0\right)^2}$$

Hence [2]

$$\theta = \left[\frac{\mathrm{R}\,\left(\mathrm{T}_1^0\right)^2\,\mathrm{M}_1}{\Delta_\mathrm{f}\mathrm{H}_1^0}\right]\,\mathrm{m_j}$$

The quantity enclosed in the […] brackets is characteristic of the solvent.

Footnotes

[1] $\theta = \mathrm{T}_1^0 - \mathrm{T}$; $\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T}_1^0} = \frac{\mathrm{T}_1^0 - \mathrm{T}}{\mathrm{T}\,\mathrm{T}_1^0} = \frac{\mathrm{T}_1^0 - \mathrm{T}}{\left(\mathrm{T}_1^0 - \theta\right)\mathrm{T}_1^0} = \frac{\theta}{\left(\mathrm{T}_1^0 - \theta\right)\mathrm{T}_1^0}$

[2] $\frac{1}{x_1} = \frac{1}{1-x_j} = \frac{1}{1-[n_j/(n_1+n_j)]} = \frac{n_1+n_j}{n_1+n_j-n_j}$ For a solution where the molality of solute $j = m_j$ $\mathrm{m_j} = \frac{\mathrm{n_j}}{\mathrm{n_1\,M_1}}$
Then, $\frac{1}{\mathrm{x_1}} = \frac{\mathrm{n_1 + n_1\,M_1\,m_j}}{\mathrm{n_1}}$
$-\ln\left[\mathrm{x}_1(\ \mathrm{s\,ln})\right] = -\ln\left[1 + \mathrm{M_1\,m_j}\right]$;
$-\ln\left[x_1(\mathrm{sln})\right] = -\ln\left[1 - x_j(s\,\mathrm{ln})\right] \approx x_j$
$x_j = \frac{m_j}{(1/M_1)+m_j} \approx m_j\,M_1$

[3] see I Prigogine and R Defay, Chemical Thermodynamics, trans. D. H. Everett, Longmans Green, London, 1953.

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1.13.7: Equilibrium - Liquid-Solids - Hildebrand Rules

A given homogeneous liquid system (at pressure p) contains two chemical substances i and j at temperature T. Chemical substance j at temperature T and p is a liquid which being in vast excess in this system is the solvent. The system is cooled and pure solid substance i separates out leaving the system less concentrated in the solute i. The solution is dilute and we assume that the thermodynamic properties of the solution are ideal. Then, from the Schroeder–van Laar Equation

$$-\ln\left[\mathrm{x_i(s\,ln)}\right] = \frac{\left[\Delta_{\mathrm{fius}}\mathrm{H_i^0}(\ \mathrm{T,p})\right]}{\mathrm{R}}\ \left[\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T_i^0}}\right] \tag{1.13.7.1}$$

$\Delta_{\mathrm{fus}}\ \mathrm{H_i^0}$ is the molar enthalpy of fusion of chemical substance i, melting point $\mathrm{T_i^0}$. Mole fraction $\mathrm{x_i(s\,ln)}$ is the composition of the saturated solution at temperature T; i.e. the solubility of substance i. From Equation 1.13.7.1,

$$\ln\left[\frac{1}{\mathrm{x_i(s\,ln)}}\right]^{\mathrm{eq}} = \frac{\left[\Delta_{\mathrm{fus}}\mathrm{H_i^0}(\ \mathrm{T,p})\right]}{\mathrm{R}}\ \left[\frac{\mathrm{T_i^0 - T}}{\mathrm{T\,T_i^0}}\right] \tag{1.13.7.2}$$

Equation 1.13.7.2 forms the background to several generalisations concerning solubilities; i.e. Hildebrand Rules [1]. We note that $\Delta_{\mathrm{fus}}\ \mathrm{H_i^0}(\ \mathrm{T,p})$ and $\mathrm{T_i^0}$ characterise the **solute**.

a. Solubilities increase with increase in temperature.
b. For two solutes with equal $\Delta_{\mathrm{fus}}\ \mathrm{H_i^0}(\ \mathrm{T,p})$, the solute with lower $\mathrm{T_i^0}$ will be more soluble at a common temperature T.
c. For two solutes with the same $\mathrm{T_i^0}$, the solid with lower $\Delta_{\mathrm{fus}}\ \mathrm{H_i^0}(\ \mathrm{T,p})$ will be more soluble.

Footnote

[1] see I. Prigogine and R. Defay, Chemical Thermodynamics, transl. D. H. Everett, Longmans Greeen, London, 1953.

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SECTION OVERVIEW

1.14: Excess and Extra Thermodynamics

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1.14.1: "Excess" Thermodynamic Properties

Description of the thermodynamic properties of both solutions and liquid mixtures in terms of excess properties has considerable merit. However care has to be exercised in defining excess properties [1- 3]. It is not sufficient, for example, to argue that all properties of a given binary liquid mixture would be linear functions of mole fraction composition in the event that the properties of this mixture are “ideal”. There is of course no rule that states one is forbidden from doing this. But it is not allowed to identify immediately deviations “ideal” with those features responsible for deviation from thermodynamically defined ideal based on, for example, Gibbs energies of mixing. Similarly it is not good practice to use an arbitrary definition of the properties of ideal solutions and to account for deviations from ideal directly in terms of fraction responsible for deviations in the thermodynamic properties of the solution from ideal.

Care has to be exercised in anticipating patterns in the properties of solutions which can be claimed as ideal from a thermodynamic viewpoint. We illustrate the point with reference to expansivities in the context of binary liquid mixtures. A given liquid mixture is prepared at defined \(\mathrm{T}\) and \(\mathrm{p}\) using \(\mathrm{n}_{1}\) moles of water and \(\mathrm{n}_{2}\) moles of liquid 2. Then,

\[\mathrm{V}(\operatorname{mix})=\mathrm{n}_{1} \, \mathrm{V}_{1}(\operatorname{mix})+\mathrm{n}_{2} \, \mathrm{V}_{2}(\operatorname{mix}) \nonumber \]

At fixed pressure (and at ‘\(\mathrm{A} = 0\)’),

\[[\partial \mathrm{V}(\mathrm{mix}) / \partial \mathrm{T}]_{\mathrm{p}}=\mathrm{n}_{1} \,\left[\partial \mathrm{V}_{1}(\mathrm{mix}) / \partial \mathrm{T}\right]_{\mathrm{p}}+\mathrm{n}_{2} \,\left[\partial \mathrm{V}_{2}(\mathrm{mix}) / \partial \mathrm{T}\right]_{\mathrm{p}} \nonumber \]

We divide through by \(\mathrm{V}(\mathrm{mix})\) and incorporate new terms.

\[\begin{aligned}
& {[1 / V(\text { mix })][\partial \mathrm{V}(\text { mix }) / \partial \mathrm{T}]_{\mathrm{p}} } \\
=& {\left[\mathrm{n}_{1} \, \mathrm{V}_{1}(\mathrm{mix}) / \mathrm{V}(\mathrm{mix})\right] \,\left[1 / \mathrm{V}_{1}(\mathrm{mix})\right]\left[\partial \mathrm{V}_{1}(\mathrm{mix}) / \partial \mathrm{T}\right]_{\mathrm{p}} } \\
&+\left[\mathrm{n}_{2} \, \mathrm{V}_{2}(\mathrm{mix}) / \mathrm{V}(\mathrm{mix})\right]\left[1 / \mathrm{V}_{2}(\mathrm{mix})\right]\left[\partial \mathrm{V}_{2}(\mathrm{mix}) / \partial \mathrm{T}\right]_{\mathrm{p}}
\end{aligned} \nonumber \]

The term \(\left[\mathrm{n}_{1} \, \mathrm{V}_{1}(\operatorname{mix}) / \mathrm{V}(\operatorname{mix})\right]\) is an effective volume fraction for substance 1, \(\phi_{1}\); similarly for \(\phi_{2}\). We define effective component expansibilities, \(\alpha_{1}\) and \(\alpha_{2}\). Thus,

\[\alpha_{1}=\left[1 / V_{1}(\mathrm{mix})\right] \,\left[\partial \mathrm{V}_{1}(\mathrm{mix}) / \partial \mathrm{T}\right]_{\mathrm{p}} \nonumber \]

and

\[\alpha_{2}=\left[1 / V_{2}(\operatorname{mix})\right] \,\left[\partial V_{2}(\operatorname{mix}) / \partial T\right]_{p} \nonumber \]

Hence (using equation (c)

\[\alpha_{p}(\operatorname{mix})=\phi_{1}(\operatorname{mix}) \, \alpha_{1}(\operatorname{mix})+\phi_{2}(\operatorname{mix}) \, \alpha_{2}(\operatorname{mix}) \nonumber \]

For an ideal mixture,

\[\mathrm{V}(\text { id:mix })=\mathrm{n}_{1} \, \mathrm{V}_{1}^{*}(\ell)+\mathrm{n}_{2} \, \mathrm{V}_{2}^{*}(\ell) \nonumber \]

Since \(\phi_{1}(\mathrm{id})\) equals \(\mathrm{n}_{1} \, \mathrm{V}_{1}^{*}(\ell) / \mathrm{V}(\mathrm{id}: \operatorname{mix})\), the volume fraction for the ideal mixture [similarly for \(\phi_{2} \text { (id) }\)], then

\[\alpha_{\mathrm{p}}(\mathrm{id}: \operatorname{mix})=\phi_{1}(\mathrm{id}) \, \alpha_{\mathrm{p} 1}^{*}(\ell)+\phi_{2}(\mathrm{id}) \, \alpha_{\mathrm{p} 2}^{*}(\ell) \nonumber \]

An excess (isobaric) thermal expansivity is given by equation (i).

\[\alpha_{p}^{E}(\operatorname{mix})=\alpha_{p}(\operatorname{mix})-\alpha_{p}(\text { id : mix }) \nonumber \]

Equation (h) confirms that

\[\alpha_{p}(\text { id : mix }) \neq \mathrm{x}_{1} \, \alpha_{\mathrm{p} 1}^{*}(\ell)+\mathrm{x}_{2} \, \alpha_{\mathrm{p} 2}^{*}(\ell) \nonumber \]

In other words the definition of an ideal property using the otherwise conventional form in equation (j) is invalid.

Footnotes

[1] M. I. Davis and G. Douheret, Thermochim. Acta,1991,**190**,267.

[2] H. L. Friedman, J.Chem.Phys.,1960,**32**,1351.

[3] R. W. Missen, Ind. Eng. Chem., Fundam.,1969,**8**,81.

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1.14.10: Extrathermodynamics - Solvent Effects in Chemical Kinetics

An enormous chemical literature describes the effects of solvents on rates of chemical reactions. C. K. Ingold [1] in his classic monograph actually uses the phrase ***'solvent polarity'*** when commenting on the relative rates of reactions through a series of solvents of diminishing ***"polarity"***. One of the reactions discussed by Ingold concerns the solvolysis of 2-chloro-2-methyl - propane, $(CH_3)_3\,CCl$. In 1948, Winstein and Grunwald [2] used this reaction as a basis for a quantitative treatment of solvent polarities leading to the definition of solvent Y-value. The basis of their analysis can be understood using an extrathermodynamic analysis [3]. We use a description based on substituent zone R and reaction zone X for a solute molecule RX. Here the interaction between the two zones is solvent dependent.

The starting point is kinetic data describing an (assumed) unimolecular first order solvolysis of a solute RX. The chemical reaction proceeds through a transition state RX^{neq}. For a given solvent medium M at defined T and p, transition state theory [9] describes the standard activation Gibbs energy as follows.

$$\Delta^{\neq}\mathrm{G}^0(\mathrm{RX};\mathrm{M}) = \mu^0\left(\mathrm{RXX}^{\neq};\mathrm{M}\right) - \mu^0(\mathrm{RX};\mathrm{M})$$

The basic postulate states that the reference chemical potential of solute RX in solution, $\mu^0(\mathrm{RX};\mathrm{sln})$ at defined T and p is given by the sum of contributions from the substituent zone, $\mu^0(\mathrm{R})$ and reaction zone , $\mu^0(\mathrm{X})$ together with terms describing the interaction of R and X with the solvent, $\mathrm{I}(\mathrm{R},\mathrm{M})$ and $\mathrm{I}(\mathrm{X},\mathrm{M})$ and the effect of solvent on this interaction $\mathrm{II}(\mathrm{R},\mathrm{X},\mathrm{M})$.

$$\begin{aligned}&\mu^0(\mathrm{RX};\ \text{in medium M}) = \\ &\quad \mu^0(\mathrm{R}) + \mu^0(\mathrm{X}) + \mathrm{I}(\mathrm{R},\mathrm{M}) + \mathrm{I}(\mathrm{X},\mathrm{M}) + \mathrm{II}(\mathrm{R},\mathrm{X},\mathrm{M})\end{aligned}$$

Thus the solvent M contributes to the interaction between R and X. A key postulate is advanced at this stage which states that the interactions terms can be factorised.

$$\begin{aligned}&\mu^0(\mathrm{X};\ \text{in medium M}) = \\ &\mu^0(\mathrm{R}) + \mu^0(\mathrm{X}) + \mathrm{I}(\mathrm{R})\,\mathrm{I}(\mathrm{M}) + \mathrm{I}(\mathrm{X})\,\mathrm{I}(\mathrm{M}) + \mathrm{II}(\mathrm{R})\,\mathrm{II}(\mathrm{X})\,\mathrm{II}(\mathrm{M})\end{aligned}$$

A similar equation is set down for the transition state.

$$\begin{aligned}&\mu^0\left(\mathrm{RX}^{\neq};\text{in medium M}\right) = \\ &\mu^0\left(\mathrm{R}^{\neq}\right) + \mu^0\left(\mathrm{X}^{\neq}\right) + \mathrm{I}\left(\mathrm{R}^{\neq}\right)\,\mathrm{I}(\mathrm{M}) + \mathrm{I}\left(\mathrm{X}^{\neq}\right)\,\mathrm{I}(\mathrm{M}) + \mathrm{II}\left(\mathrm{R}^{\neq}\right)\,\mathrm{II}\left(\mathrm{X}^{\neq}\right)\,\mathrm{II}(\mathrm{M})\end{aligned}$$

Equations (c) and (d) are combined with equation (a). For reaction in solvent medium M,

$$\begin{aligned}&\Delta^{\neq}\mathrm{G}^0(\mathrm{RX},\mathrm{M}) = \\ &\left[\mu^0\left(R^{\neq}\right) - \mu^0(R)\right] + \left[\mu^0\left(X^{\neq}\right) - \mu^0 X\right] \\ &+ \mathrm{I}(\mathrm{M})\,\left[\mathrm{I}\left(\mathrm{R}^{\neq}\right) - \mathrm{I}(\mathrm{R})\right] + \mathrm{I}(\mathrm{M})\,\left[\mathrm{I}\left(\mathrm{X}^{\neq}\right) - \mathrm{I}(\mathrm{X})\right] \\ &+ \mathrm{II}(\mathrm{M})\,\left[\mathrm{II}\left(\mathrm{R}^{*}\right)\,\mathrm{II}\left(\mathrm{X}^{\neq}\right) - \mathrm{II}(\mathrm{R})\,\mathrm{II}(\mathrm{X})\right]\end{aligned}$$

A second postulate state that $\mathrm{II}(\mathrm{M})$ and $\mathrm{I}(\mathrm{M})$ are simply related; i.e. equation (f).

$$\mathrm{II}(\mathrm{M}) = \alpha\,\mathrm{I}(\mathrm{M})$$

If $\Delta_m\Delta^{\neq}G^0(\mathrm{RX})$ describes the effect of solvent M on $\Delta^{\neq}\mathrm{G}^0(\mathrm{RX})$, $\Delta_\mathrm{m}\Delta^{\neq}\mathrm{G}^0(\mathrm{RX})$ is given by the product of a (solvent operator) and a (substrate operator). By definition,

$$\Delta_\mathrm{m}\Delta^{\pm}\mathrm{G}^0(\mathrm{RX}) = \Delta_\mathrm{m}\mathrm{Y}\left(\text{ substrate operator }\right)$$

Originally the substrate operator was set to unity for $(CH_3)_3\,CCl$, and Y was set to zero for an 80:20 ethanol + water mixture [4]. The outcome was a set of Y-values for many solvents, particularly alcohol + water mixtures at $298.5\ \mathrm{K}$ and ambient pressure

Footnotes

[1] C. K. Ingold, Structure and Mechanism in Organic Chemistry, G. Bell, London, 1953; see page 347.

[2] E. Grunwald and S. Winstein, J. Am. Chem. Soc., 1948,**70**, 841; 846.

[3] J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, New York, 1963; Dover Publications , New York,1989.

[4] $20\ \mathrm{cm}^3$ of ethanol(ℓ) was poured from a volumetric flask containing $1\ \mathrm{dm}^3$ of ethanol(ℓ). The liquid in the flask was then 'topped up' with water(ℓ). The mixture is a good solvent for both apolar and polar solutes. Unfortunately the exact composition of the mixture is unknown. As rarely stated, the volume of water required is slightly larger than $20\ \mathrm{cm}^3$. Professor Ross E Robertson (University of Calgary) viewed with interest that so much information in the chemical literature describes rates of chemical reactions where the solvent is vodka.

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1.14.2: Excess Thermodynamic Properties - Liquid Mixtures

A given liquid mixture at temperature T and pressure p ($\cong \mathrm{p}^0$) contains i-liquid chemical substances. The chemical potential of liquid component j is given by equation (a) where $\mu_{\mathrm{j}}^*(\ell)$ is the chemical potential of liquid component j at the same T and p.

$$\mu_{\mathrm{j}}(\mathrm{mix}) = \mu_{\mathrm{j}}^*(\ell) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{x}_{\mathrm{j}}\,\mathrm{f}_{\mathrm{j}}\right)$$

Here $\mathrm{limit}\,(\mathrm{x}_{\mathrm{j}} \rightarrow 1)\,\mathrm{f}_{\mathrm{j}} = 1.0$ at all T and p.

If the thermodynamic properties of the liquid mixture are ideal,

$$\mu_j(\mathrm{mix;id}) = \mu_{\mathrm{j}}^*(\ell) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{x}_{\mathrm{j}}\right)$$

The excess chemical potential for liquid substance j,

$$\mu_{\mathrm{j}}^{\mathrm{E}}(\mathrm{mix}) = \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{f}_{\mathrm{j}}\right)$$

DSF

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1.14.3: Excess Thermodynamic Properties- Aqueous Solutions

A given aqueous solution, at temperature T and pressure p ($\cong \mathrm{p}^0$), contains i-solutes, with $\mathrm{n_j}$ moles of each solute j, and $\mathrm{n_1}$ moles of water(ℓ).The Gibbs energy of the solution is given by equation (a).

$$\mathrm{G(aq) = n_1\,\mu_1(aq) + \sum_{j=1}^{j=i} n_j\,\mu_j(aq)}$$

For a solution prepared using $1\ \mathrm{kg}$ of water(ℓ), in vast molar excess,

$$\mathrm{G\,(aq; w_1 = 1\ kg) = (1/M_1)\ \mu_1(aq) + \sum_{j=1}^{s} m_j\,\mu_j(aq)}$$

We assert that the system is at thermodynamic equilibrium. For each solute j, $\mu_j(\mathrm{aq})$ is related to the molality $\mathrm{m_j}$ and the reference chemical potential for solute j in a solution where $\mathrm{m_j = 1\ molkg^{-1}}$ and the thermodynamic properties of the solute are ideal. Then,

$$\left\{\mathrm{m^0 = 1\ mol\ kg^{-1}}\right\} \quad \mu_j(\mathrm{aq}) = \mu_j^0(\mathrm{aq}) + \mathrm{R\,T\,ln\left(m_j\,\gamma_j/m^0\right)}$$

where $\mathrm{limit}\,(m_j \to 0)\,\gamma_j = 1.0$ at all T and p.

For the solvent we express the properties in terms of a practical osmotic coefficient, ϕ.

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - \phi\,\mathrm{R\,T\,M_1}\sum_{j=1}^{j=i} \mathrm{m_j}$$

At all T and p, $\mathrm{limit}\left(\sum_{j=1}^{j=i} m_j \to 0\right)\phi = 1.0$

For the solution,

$$\mathrm{G\,(aq; w_1 = 1\ kg) = (1/M_1)}\left[\mu_1^*(\ell) - \phi\,\mathrm{R\,T\,M_1}\sum_{j=1}^{j=i}\mathrm{m_j}\right] + \sum_{j=i}\mathrm{m_j}\ \left[\mu_j^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_j\,\gamma_j/m^0\right)}\right]$$

If the thermodynamic properties of the solution are ideal,

$$\mathrm{G\,(aq; id; w_1 = 1\ kg) = (1/M_1)}\left[\mu_1^*(\ell) - \mathrm{R\,T\,M_1}\sum_{j=1}^{j=i}\mathrm{m_j}\right] + \sum_{j=1}^{j=i}\mathrm{m_j}\ \left[\mu_j^0(\mathrm{aq}) + \mathrm{R\,T\ ln\left(m_j/m^0\right)}\right]$$

By definition the solution excess Gibbs energy of the solution,

$$\mathrm{G^E\,(aq; w_1 = 1\ kg) = G\,(aq; w_1 = 1\ kg) - G\,(aq; id; w_1 = 1\ kg)}$$

$\mathrm{G^E\,(aq; w_1 = 1\ kg)}$ is expressed in $\left[\mathrm{Jkg^{-1}}\right]$.

Then

$$\mathrm{G^E\,(aq; w_1 = 1\ kg) = (1/M_1)\ R\,T\,M_1\,(1-\phi)}\sum_{j=1}^{j=i}\mathrm{m_j} + \sum_{j=1}^{j=i}\mathrm{m_j\,R\,T\ ln\,(\gamma_j)}$$

$$\mathrm{G^E\,(aq; w_1 = 1\ kg)\,/R\,T = (1-\phi)}\sum_{j=1}^{j=i}\mathrm{m_j} + \sum_{j=1}^{j=i}\mathrm{m_j\ ln\,(\gamma_j)}$$

For a solution containing a single solute j,

$$\mathrm{G^E\,(aq; w_1 = 1\ kg)\,/R\,T = [1-\phi+ln\,(\gamma_j)]\ m_j}$$

If the thermodynamic properties of the solution are ideal, the chemical potential of the solute is given by equation (k).

$$\mu_j(aq;id) = \mu_j^0(aq) + R\,T\,\ln\left(m_j/m^0\right)$$

Equation (c) describes the properties of solute j in a real solution. By definition the excess chemical potential $\mu_j^E(aq)$ is given by equation (l).

$$\mu_j^E(aq) = \mu_j(aq) - \mu_j(aq;id)$$

Then,

$$\mu_j^E(aq) = R\,T\,\ln\left(\gamma_j\right)$$

Often an excess chemical potential $\mu_j^E(aq)$ is written in the form G_j^E. In the case of the solvent, water(ℓ) the corresponding equations for the chemical potentials in solutions having either real or ideal thermodynamic properties are given by equations (n) and (o).

$$\mu_1(aq;id) = \mu_1^*(\ell) - R\,T\,M_1\,m_j$$

$$\mu_1(aq) = \mu_1^*(\ell) - \phi\,R\,T\,M_1\,m_j$$

$$\mu_1^E(aq) = (1-\phi)\,R\,T\,M_1\,m_j$$

Footnotes

[1] For further comments see—

a. M. I. Davis and G. Douheret, Thermochim. Acta, 1991,**190**,267.
b. H. L. Friedman, J. Chem.Phys.,1969,**32**,1351.

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1.14.4: Extensive and Intensive Variables

The terms, variables and properties are synonymous. Nevertheless a given thermodynamic property of a system can be classified as either intensive or extensive.

Intensive Properties. The magnitude of an intensive variable does NOT depend on the amount of chemical substance in a given closed system; e.g. density.

Extensive Properties. The magnitude of an extensive variable depends on the amount of chemical substances in a closed system; e.g. volume. Let us ask – is temperature an intensive or extensive variable? Consider two conical flasks. Flask A contains $10\ \mathrm{cm}^3$ of water(ℓ) at $298\ \mathrm{K}$. Flask B contains $5\ \mathrm{cm}^3$ of water(ℓ) at $298\ \mathrm{K}$. The contents of Flask are poured into Flask B.

i. What is the volume of liquid in flask B? The answer is clearly $15\ \mathrm{cm}^3$.
ii. What is the temperature of the liquid in flask B? Based on the answer to the previous question, we might answer $596\ \mathrm{K}$, being the sum $298 + 298$. This is clearly wrong. We have not distinguished between extensive variable variable and the intensive variable temperature. Temperature is an intensive variable as, for example, is the density of liquids.
iii. A quick test to decide whether a given variable is either extensive or intensive is to ask what happens to the number value if the amount of chemical substance in a system increases by a factor of two. If the variable (e.g. volume) also increases by a factor of two, the variable is extensive. If the variable (e.g. temperature, equilibrium constant…) remains unchanged , the variable is intensive. Otherwise the variable is neither extensive nor intensive (e.g. the inverse of volume).

Footnote

[1] O. Redlich (J. Chem.Educ.,1970,**42**,154) presents a provocative discussion of the distinction between intensive and extensive variables.

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1.14.5: Extent of Reaction

For chemists, chemical reaction is the key thermodynamic process. By definition chemical reaction produces a change in composition of a closed system. The extent of chemical reaction is measured by a quantity $\mathrm{d}\xi$, where the chemical composition is described by the symbol ξ. An example makes the point.

An aqueous solution is prepared at temperature T and pressure p contains solute X. The latter undergoes spontaneous chemical reaction to form chemical substance Y.

Thus

	$\mathrm{X(aq)}$	$\rightarrow$	$\mathrm{Y(aq)}$
At $t = 0$	$\mathrm{n_X^0}$		$0\ \mathrm{mol}$
At time t,	$\mathrm{n_X^0} - \xi$		$\xi\ \mathrm{mol}$
Rate of reaction	$= \mathrm{d}\xi/\mathrm{dt}$		

[Time is a legitimate thermodynamic property.]

A key concept states that spontaneous chemical reaction is driven by the affinity for spontaneous change, A. Then by definition equilibrium corresponds to the state where $\mathrm{A} = 0$, and $\mathrm{d}\xi/\mathrm{dt} = 0$.

General Terms

For a system containing i-chemical substances, the chemical potential of chemical substance j is given by equation (a).

$$\mu_\mathrm{j} = \left(\frac{\partial \mathrm{G}}{\partial n_\mathrm{j}}\right)_{\mathrm{T,p,n(i\neq j)}}$$

Then,

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mu_\mathrm{j}\,\mathrm{dnj_j}$$

But,

$$\mathrm{dG} = -\mathrm{S}\,\mathrm{dT} + \mathrm{V}\,\mathrm{dp} - \mathrm{A}\,\mathrm{d}\xi$$

By comparison,

$$A\,d\xi = -\sum_{j=1}^{j=i} \mu_j\,dn_j$$

But $\mathrm{dn_j} = \mathrm{v_j}\,\mathrm{d}\xi$ where ν_j is positive for products and negative for reactants. Hence,

$$A = -\sum_{j=1}^{j=i} v_j\,\mu_j$$

This remarkable equation relates the affinity for chemical reaction A with the chemical potentials of the chemical substances involved in the chemical reaction. Moreover at equilibrium, A is zero. Hence,

$$\sum_{j=1}^{j=i} v_j\,\mu_j^{eq} = 0$$

We have a condition describing chemical equilibrium in terms of the chemical potentials of reactants and products at equilibrium.

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1.14.6: Extent of Reaction - General

The variable ξ describes in quite general terms the molecular composition/organisation. For a closed system at fixed T and p, there is a composition/organisation ξ^{eq} corresponding to a minimum in Gibbs energy where the affinity for spontaneous change is zero. In general terms there is an extent of reaction ξ corresponding to a given affinity A at defined T and p. In fact we can express ξ as a dependent variable defined by the independent variables T, p, and A. Thus

$$\xi = \xi[\mathrm{T}, \mathrm{p}, \mathrm{A}]$$

The general differential takes the following form.

$$\mathrm{d}\xi = \left(\frac{\partial \xi}{\partial T}\right)_{\mathrm{p,A}} \mathrm{dT} + \left(\frac{\partial \xi}{\partial \mathrm{p}}\right)_{\mathrm{p,A}} \mathrm{dp} + \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T,p}} \mathrm{dA}$$

The change in chemical composition occurs spontaneously. The change in composition is described in terms of the extent of chemical reaction, ξ. In a given aqueous solution, the chemical reaction is:

$$\mathrm{CH_3COOC_2H_5} + \mathrm{OH^-(aq)} \rightarrow \mathrm{CH_3COO^-(aq)} + \mathrm{C_2H_5OH(aq)}$$

At each stage the **extent of chemical reaction** is represented by the symbol ξ [1].

$$\mathrm{CH_3COOC_2H_5(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{CH_3COO^-(aq)} + \mathrm{C_2H_5OH(aq)}$$

At $t = 0$ (i.e. as prepared)

$$n(\text{ ester })^0 \quad n\left(\mathrm{OH^-}\right)^0 \quad 0 \quad 0$$

After extent of reaction ξ (at some time later)

$$n(\text{ ester })^0 - \xi \quad n\left(\mathrm{OH^-}\right)^0 - \xi \quad \xi \quad \xi$$

As the reaction proceeds so ξ increases. [NB The zero superscript signals ‘at time zero’.] At a given stage of the reaction and time t, (accepting dt is positive), Rate of Reaction = $\mathrm{d}\xi/\mathrm{dt}$

We now ask ‘why did chemical reaction proceed in this direction?’. The answer is ---- the chemical reaction was driven by the affinity for spontaneous change, symbol A. By identifying these two ideas, affinity for spontaneous change and the rate of reaction $\mathrm{d}\xi/\mathrm{dt}$, we arrive at two important criteria for **chemical equilibrium**.
Affinity for spontaneous change $\mathrm{A} = 0$
Rate of change $\mathrm{d}\xi/\mathrm{dt} = 0$

However we need to stand back a little and examine how we might advance generalizations concerning the direction of **Spontaneous Chemical Reaction**. What macroscopic property can be identified which accounts for the fact that alkaline hydrolysis of ethyl ethanoate is spontaneous? To make further progress we introduce two laws of thermodynamics. Actually these are not laws in the sense of being laid down by government or by religious doctrine. Rather these laws are AXIOMS. We explore these axioms in the context for which ξ refers to a change in composition resulting from chemical reaction [2].

Footnotes

[1] For a discussion of the significance of extent of reaction ξ, see:

a. K. J. Laidler and N. Kallay, Kem. Ind. (Sofia) 1988, **37**, 182.
b. F. R. Cruikshank, A. J. Hyde and D. Pugh, J.Chem.Educ., 1977, **54**, 88.
c. P. G. Wright, Educ. Chem., 1986,**23**, 111.
d. M. J. Blandamer, Educ. in Chem.,1999,**36**,78.

[2] The usefulness of the concept of extent of chemical reaction ξ is further illustrated by the following examples.

A. A closed system (at fixed temperature T and pressure p) is prepared using $\mathrm{n_x^0}$ moles of chemical substance X in $\mathrm{w_1\ kg}$ of solvent,

water. Spontaneous chemical reaction forms chemical substances Y and \(\mathrm{Z}\).

Thus,	2X	$\rightarrow$ 3Y	+ Z
At $t = 0$	$\mathbf{n}_X^0$	0	0 mol
After extent of reaction, ξ with $\mathbf{n}_X^0$	$\mathrm{n_x^0} - 2.\xi$	$3.\xi$	$2.\xi$ mol

B. If the chemical reaction in (A) proceeds to completion,

2X	$\rightarrow$ 3Y	+ Z
0	$3\,n_x^0/2$	$\mathrm{n_x^0}/2$ mol

C. If the chemical reaction in examp1e (A) proceeds to chemical equilibrium, then with \(\xi = \xi^{\mathrm{eq}}\),

	2X $\rightleftarrows$	3Y+	Z
Amounts	$\mathrm{n_x^0} - 2\,\xi^{\mathrm{eq}}$	$\mathrm{n_x^0} - 2\,\xi^{\mathrm{eq}}$	$3\,\xi^{\mathrm{eq}}$ mol
Molalities	$(n_x^0 - 2\,\xi^{eq})\,/w_1$	$3\,\xi^{\mathrm{eq}}/\mathrm{w_1}$	ξ^{eq}/w_1 molkg^{-1}

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1.14.7: Extrathermodynamics - Background

Essentially thermodynamics is used to analyze experimental data. In these terms, thermodynamics shows how properties of systems are related and how one can link measured properties with important thermodynamic variables. Nevertheless, there are cases where a pattern seems to emerge from measured variables which is not a consequence of the laws of thermodynamics. Furthermore, it is often discovered that the patterns can actually be accounted for if one or two additional postulates are made. These new postulates are therefore extra-thermodynamic and the analytical method is called **extrathermodynamics** [1,2]. The analysis has merit in that the new postulates point to patterns which can be developed for other systems.

The essence of the argument can be understood by considering the molar volume of pure ethanol at ambient pressure and $298.2\ \mathrm{K}$. Clearly Extra \left or missing \right is a properly defined thermodynamic variable. But as chemists we might be tempted to explore an extrathermodynamic postulate in which $\mathrm{V}^{*}\left(\mathrm{C_2H_5OH};\ell\right)$ can be subdivided into group contributions. Thus

$$\mathrm{V}^{*}\left(\mathrm{C_2H_5OH};\ell\right)=\mathrm{V}\left(\mathrm{CH_3}\right)+\mathrm{V}\left(\mathrm{CH_2}\right)+\mathrm{V(OH)} \tag{1.14.7.1}$$

This equation cannot be justified on thermodynamic grounds. Nevertheless we might examine molar volumes of several (liquid) alcohols at the same T and p and come up with a self-consistent set of group volumes. For example,

$$\left[\mathrm{V}^{*}\left(\mathrm{n-C_3H_7OH};\ell\right)\right]=\mathrm{V}\left(\mathrm{CH_3}\right)+2*\ \mathrm{V}\left(\mathrm{CH_2}\right)+\mathrm{V(OH)} \tag{1.14.7.2}$$

Hence comparison of Equations 1.14.7.1 and 1.14.7.2 yields directly $\mathrm{V}\left(\mathrm{CH_2}\right)$, the contribution of methylene groups to the molar volume of (liquid) alcohols at the same T and p. Although such an analysis might be judged naïve, the general approach finds merit in several subject areas; e.g chemical equilibria and chemical kinetics.

Footnotes

[1] J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, London, 1963.

[2] E. Grunwald, Thermodynamics of Molecular Species, Wiley, New York, 1997.

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1.14.8: Extrathermodynamics - Equilbrium - Acid Strength

In aqueous solution at ambient pressure and $298.15\ \mathrm{K}$, benzoic acid exists in the form of a chemical equilibrium described in equation (a)

$$\mathrm{PhCOOH(aq)} \Leftrightarrow = \mathrm{H^+(aq) + PhCOO^-(aq)}$$

At defined T and p,

$$\Delta_\mathrm{r} \mathrm{G}^0(\mathrm{PhCOOH;aq}) = \mu^0\left(\mathrm{PhCOO^-;aq}\right) + \mu^0\left(\mathrm{H^+;aq}\right) - \mu^0(\mathrm{PhCOOH;aq})$$

In the case of a substituted benzoic acid, $\mathrm{XC_6H_4COOH} \quad [= \mathrm{XPhCOOH}]$, the corresponding description of the chemical equilibrium takes the following form.

$$\begin{aligned}&\Delta_\mathrm{r} \mathrm{G}^0(\mathrm{XPhCOOH;aq}) \\ &= \mu^0(\mathrm{XPhCOO;;aq}) + \mu^0\left(\mathrm{H^+;aq}\right) - \mu^0(\mathrm{XPhCOOH;aq})\end{aligned}$$

In aqueous solution at ambient pressure and $298.15\ \mathrm{K}$, the properties of an aqueous solution containing phenol can be described in terms of the following equilibrium.

$$\mathrm{PhOH(aq)} \Leftrightarrow \Longrightarrow \mathrm{H^+(aq) + PhO^-(aq)}$$

Then, (cf. equation (b)),

$$\Delta_\mathrm{r} \mathrm{G}^0(\mathrm{PhOH;aq}) = \mu^0\left(\mathrm{PhO^-;aq}\right) + \mu^0\left(\mathrm{H^+;aq}\right) - \mu^0(\mathrm{PhOH;aq})$$

In the case of a substituted phenol XPhOH, the equation corresponding to equation (d) takes the following form.

$$\Delta_\mathrm{r} \mathrm{G}^0(\mathrm{XPhOH;aq}) = \mu^0\left(\mathrm{XPhO^-;aq}\right) + \mu^0\left(\mathrm{H^+;aq}\right) - \mu^0(\mathrm{XPhOH;aq})$$

In the following we compare situations where X is common to the substituted phenol and benzoic acid including position in the aromatic ring. The interesting point to emerge is that for a range of substituents, X, the recorded dependence of $\Delta_{\Delta_\mathrm{r}} \mathrm{G}^0(\mathrm{XPhOH;aq})$ on $\Delta\Delta_\mathrm{r} \mathrm{G}^0(\mathrm{XPhCOOH;aq})$ is linear. Such a pattern is not a requirement of thermodynamics [1]. The challenge is to suggest a set of minimum relationships which account for this pattern [2,3].

Zone Model POSTULATE---Single Interaction Mechanism

Consider the reference chemical potential for solute RX in aqueous solution at fixed T and p, $\mu^0(\mathrm{RX;aq})$. As chemists we recognise that groups R and X do not make independent contributions to $\mu^0(\mathrm{RX;aq})$ [4]. The postulate, Single Interaction Mechanism, recognises that the groups R and X interact such that $\mu^0(\mathrm{RX;aq})$ is given by equation (g).

$$\mu^0(\mathrm{RX;aq}) = \mu^0(\mathrm{R}) + \mu^0(\mathrm{X}) + \mathrm{I(R,X)}$$

Here symbol R identifies the substituent zone and X identifies the reaction zone so that $\mathrm{I(R,X)}$ describes interaction between these two zones.

Separability Postulate

The interaction variable $\mathrm{I(R,X)}$ is a function of scalar variables. Then

$$\mu^0(\mathrm{RX;aq}) = \mu^0(\mathrm{R}) + \mu^0(\mathrm{X}) + \mathrm{I(R)\,I(X)}$$

Hence for benzoic acid $\mathrm{PhCOOH(aq)}$,

$$\mu^0(\mathrm{PhCOOH;aq}) = \mu^0(\mathrm{Ph}) + \mu^0(\mathrm{COOH}) + \mathrm{I(Ph)\,I(COOH)}$$

Similarly,

$$\mu^0(\mathrm{PhCOO;;aq}) = \mu^0(\mathrm{Ph}) + \mu^0\left(\mathrm{COO^-}\right) + \mathrm{I(Ph)\,I\left(COO^-\right)}$$

Hence,

$$\Delta_r G^0(\mathrm{PhCOOH;aq}) = \mu^0(\mathrm{Ph}) + \mu^0\left(\mathrm{COO^-}\right) + \mathrm{I(Ph)\,I\left(COO^-\right)} + \mu^0\left(\mathrm{H^+}\right)$$
$$-\mu^0(\mathrm{Ph}) - \mu^0(\mathrm{COOH}) - \mathrm{I(Ph)\,I(COOH)}$$

Or,

$$\Delta_r G^0(\mathrm{PhCOOH;aq}) = \mu^0\left(\mathrm{COO^-}\right) + \mathrm{I(Ph)\,I\left(COO^-\right)} + \mu^0\left(\mathrm{H^+}\right)$$
$$-\mu^0(\mathrm{COOH}) - \mathrm{I(Ph)\,I(COOH)}$$

A similar equation emerges describing the acid dissociation of the substituted acid. Thus,

$$\Delta_r G^0(\mathrm{XPhCOOH;aq}) = \mu^0\left(\mathrm{COO^-}\right) + \mathrm{I(XPh)\,I\left(COO^-\right)} + \mu^0\left(\mathrm{H^+}\right)$$
$$-\mu^0(\mathrm{COOH}) - \mathrm{I(XPh)\,I(COOH)}$$

By definition,

$$\Delta_r G^0 = \Delta_r G^0(\mathrm{XPhCOOH;aq}) - \Delta_r G^0(\mathrm{PhCOOH;aq})$$

Hence,

$$\Delta\Delta_r G^0(\text{ acids }) = \left[\mathrm{I(XPh)\,I\left(COO^-\right) - I(XPh)\,I(COOH)}\right]$$
$$-\left[\mathrm{I(Ph)\,I\left(COO^-\right) - I(Ph)\,I(COOH)}\right]$$

Or,

$$\Delta\Delta_r G^0(\text{ acids }) = \left[\mathrm{I(XPh) - I(Ph)}\right]\,\left[\mathrm{I\left(COO^-\right) - I(COOH)}\right]$$

Thus $\Delta_r G^0$ is given by the product of two terms;

i. a difference in substituent parameters, and
ii. a difference in reaction zone parameters.

We turn our attention to the acid strength of phenol and susbstituted phenols in aqueous solution at the same T and p. A similar analysis to that set out above yields the following equation.

\[G (phenols) [I(XPh) I(Ph)] [I(O) I(OH)] 0 ΔΔr = − · − − (q)

Comparison of equations (p) and (q) yields equation (r).

$$\Delta\Delta_r G^0(\text{ phenols }) = \Delta\Delta_r G^0\left(\text{acids }\right)\,\left\{\left[\mathrm{I\left(O^-\right) - I(OH)}\right] / \left[\mathrm{I\left(COO^-\right) - I(COOH)}\right]\right\}$$

The analysis rationalises the observation that $\Delta\Delta_r G^0\left(\text{phenols}\right)$ is a linear function of $\Delta\Delta_r G^0\left(\text{acids}\right)$. In other words we have not **proved** that such a linear function exists. Rather we have identified the minimum hypothesis required to account for the observation. In these terms the extrathermodynamic analysis has pointed to a reason for the recorded dependences of $\Delta\Delta_r G^0\left(\text{phenols}\right)$ on $\Delta\Delta_r G^0\left(\text{acids}\right)$. The pattern is not a requirement of thermodynamics.

Footnotes

[1] See for example,

a. D. T. Y. Chen and K. J. Laidler, Trans. Faraday Soc., 1962, **58**, 486.; and
b. C. M. Judson and M. L. Kilpatrick, J. Am. Chem. Soc., 1949, **71**, 3115.

[2] J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, London, 1963.

[3] E. Grunwald, Thermodynamics of Molecular Species, Wiley, New York, 1997.

[4] The superscript '0' is retained although the meaning here is somewhat obscure. It effectively reminds us that we are dealing with the properties of a solute in its solution reference state.

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1.14.9: Extrathermodynamics - Solvent Polarity

A solution comprises at least two chemical substances, solvent and solute. The amount of solvent far exceeds the amount of solute so in this sense a solute is dispersed through a solvent [1,2]. Although the solvent molecules are in vast excess, our interest centres on the minor (solute) component because chemists attempt to understand how interactions between a solute molecule and surrounding solvent molecules control the properties of the solute molecule; *e.g.* control reactivity, solubility, and colour [3]. Out of this interest in solute - solvent interactions emerges the concept of ***solvent polarity*** which attempts to characterise this interaction [4].

The general concept of ***solvent polarity*** can be understood by considering developments in two subjects;

i. Chemical Kinetics,
ii. Spectro-photometry.

We review briefly each of these subject areas, indicating how the concept of polarity and/or solvent polarity emerged. We show how the intuitive concept of solvent polarity in these subject areas developed in quantitative terms. We used the word ***intuitive*** and this usage can be understood in the following terms. Asked to prepare a solution of sodium chloride (table salt), a first year freshman student would choose ***water*** as the solvent rather than (liquid) benzene or ethanol because (the student would argue) water is more "polar" than either ethanol or benzene. Here the term "polar" is little more than laboratory jargon. We seek a quantitative measure of solvent polarity.

Y-values

In 1862 Bertholet and Pean de Saint Gilles noted that the rate of chemical reaction depends on the solvent. In 1890, Menschutkin confirmed that finding in a very detailed study. So for more than 100 years chemists have attempted to describe quantitively these solvent effects. Perhaps not suprisingly the first attempts concentrated on the dependendence of rate constants on the relative permittivity of solvents. Many authors sought correlations using the treatments described by Kirkwood [5-8]. The quantity used in these correlations usually takes the form $(\varepsilon_r - 1) / (2\,\varepsilon_r + 1)$. But as many authors point out, this Kirkwood function is little better than the relative permittivity for describing interactions at the molecular level. Nevertheless the challenge remained to describe kinetic solvent effects. A particular important stage was the growth of interest in physical organic chemistry [9]. Probably the ‘father’ of this subject was C.K.Ingold. In his classic monograph [9] , Ingold actually used the pharase ‘solvent polarity’when commenting on the rates of reactions through a series of - 1 - solvents of diminishing polarity; water, ethanol, propanone, benzene. But Ingold did not offer a polarity scale. One of the reactions discussed by Ingold was the hydrolysis of $(CH_3)_3\,CCl$.

$$(CH_3)_3\,CCl(aq) + H_2O(aq) \rightarrow (CH_3)_3\,COH(aq) + H^+(aq) + Cl^-(aq)$$

This classic reaction (although the mechanism is still debated) formed the basis of a quantitative description of solvent polarity described by Winstein and coworkers [10,11]. Using the rate of reaction described above they identified a reference solvent, a mixture formed by ethanol (80 vol%) and water(20 vol%). If the rate constant for this reaction is k^0 in this solvent mixture and the rate constant is k in a new solvent, the Y-value of this new solvent is given by

$$Y = \log\left(k/k^0\right)$$

In effect Y measures the ionising power of the solvent – the extent to which the solvent favours charge separation within the neutral solute. Hence by measuring the rate constant for the above reaction in a given solvent, the polarity of the solvent is obtained as shown by its Y-value.

This kinetic approach to the determination of solvent polarities has attracted attention, particularly in the context probing reaction mechanisms [9-12]. The Y-value approach can be rationalised using an extrathermodynamic analysis [13]. Nevetheless application of the solvent polarity scale based on Y-values is limited. The range of solvents for which Y-values can be measured is restricted.

Z-values

A feature of many dye molecules is the sensitivity of their colour to the solvent. This fact was exploited by Brooker and coworkers who used two dyes to define χ_B and χ_R values [14]. These scales have not found wide application. A polarity which has attracted attention was suggested by Kosower [15,16]. The scale is based on the uv/visible spectra of N-methyl pyridinium iodide. The low

energy absorption band in the spectra characterises the charge transfer from iodide to the pyridinium ring. Kosower examined correlations between Z – and Y- values and between Z-values and other solvent sensitive partaneters . The consensus is that Z provides a reasonable sastifactory measure of solvent polarity.

E_T Values

There can be little doubt that chemists find the concept of **solvent polarity** intuitively attractive . Granted the need there is an associated demand for a convenient, readily available method for measuring solvent polarity. Reichardt synthesised a betaine dye which - 2 - is particularly solvent sensitive as shown by the dependence on solvent of an intramolecular charge transfer band [17]. Reichardt expresses the energy of the energy band maximum of the absorption band in kilocalories per mol which defines the E_T value for a given solvent. Solutions of the dye in methanol are red, violet in ethanol and green in propanone. So one has a striking visual indicator of solvent polarity.

Foonotes

[1] In a solution which is defined as ideal in a thermodynamic sense there are no (solute molecule) $\leftrightarrow$ (solute molecule) interactions. Hence the solute molecules are effectively infinitely far apart.

[2] Some indication of the ratio of solute to solvent molecules is indicated by the following rough calculation. Dilute aqueous solutions used in a study of chemical kinetics have concentrations of approx. $10^{-3}\mathrm{moldm}^{-3}$. In $1\mathrm{dm}^3$ of water there are 55.5 moles of water so the ratio of solute to solvent molecules is around 55000.

[3] Although the term is not used by chemists it may be helpful to imagine each solute molecule ***bathed*** in solvent molecules, implying a limitless expanse of solvent molecules around each solute molecule.

[4] We confine attention to the properties of solvents (*e.g.* polarities) at ambient pressure and at $298.2\ \mathrm{K}$; i.e. 25 Celsius which is just above conventional room temperature.

[5] J.G.Kirkwood, J. Chem. Phys.,1934,**2**,351.

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[7] See comments by N. S. Isaacs, Physical Organic Chemistry, Longmans, London,1987.

[8] See also comments concerning attempts to identify a single solvent property which accounts for solvent effects on rates of chemical reactions; J. B. F. N. Engberts, in Water-A Comprehensive Treatise, ed. F.Franks, Plenum Press, New York, 1979,Volume 6, chapter 4.

[9] C.K.Ingold, Structure and Mechanism in Organic Chemistry, G. Bell, London, 1953; see page 347.

[10]

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SECTION OVERVIEW

1.15: Heat Capacities

Topic hierarchy

1.15.1: Heat Capacities: Isobaric: Neutral Solutes

1.15.2: Heat Capacities: Solutions: Solutes: Interaction Parameters

1.15.3: Heat Capacities: Isobaric: Solutions: Unit Volume

1.15.4: Heat Capacities: Isobaric: Salt Solutions

1.15.5: Heat Capacities: Isochoric: Liquid Mixtures: Ideal

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1.15.1: Heat Capacities: Isobaric: Neutral Solutes

An aqueous solution molality m_j, at temperature T and pressure p, contains a simple neutral solute, j. The chemical potential of the solute is given by equation (a).

$$\mu_{\mathrm{j}}\left(\mathrm{aq};\mathrm{m_j};\mathrm{T};\mathrm{p}\right) = \\ \mu_{\mathrm{j}}^{0}\left(\mathrm{aq};\mathrm{T};\mathrm{p}^{0}\right) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right) + \int_{\mathrm{p}^{0}}^{\mathrm{p}} \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T})\,\mathrm{dp}$$

$$\mathrm{H_j}\left(\mathrm{aq};\mathrm{m_j};\mathrm{T};\mathrm{p}\right) = \mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) - \mathrm{R}\,\mathrm{T}^{2}\left[\partial \ln\left(\gamma_{\mathrm{j}}\right)/\partial \mathrm{T}\right]_{\mathrm{p}}$$

where

$$\mathrm{limit}\left(\mathrm{m_j} \to 0\right) \mathrm{H_j}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p})$$

$$\mathrm{C_{pj}}\left(\mathrm{aq};\mathrm{m_j};\mathrm{T};\mathrm{p}\right) = \\ \mathrm{C}_{\mathrm{pj}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) - 2\,\mathrm{R}\,\mathrm{T}\left[\partial \ln\left(\gamma_{\mathrm{j}}\right)/\partial \mathrm{T}\right]_{\mathrm{p}} - \mathrm{R}\,\mathrm{T}^{2}\left[\partial^{2} \ln\left(\gamma_{\mathrm{j}}\right)/\partial \mathrm{T}^{2}\right]_{\mathrm{p}}$$

Here

$$\mathrm{C}_{\mathrm{pj}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \left[\partial \mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{aq})/\partial \mathrm{T}\right]_{\mathrm{p}}$$

For the solvent, the chemical potential is given by equation (f).

$$\mu_1\left(\mathrm{aq};\mathrm{m_j};\mathrm{T};\mathrm{p}\right) = \mu_1^{0}\left(\ell;\mathrm{T};\mathrm{p}^{0}\right) - \phi\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j} + \int_{\mathrm{p}^{0}}^{\mathrm{p}} \mathrm{V}_1^{*}(\ell;\mathrm{T})\,\mathrm{dp}$$

$$\mathrm{H}_1\left(\mathrm{aq};\mathrm{m_j};\mathrm{T};\mathrm{p}\right) = \mathrm{H}_1^{*}(\ell;\mathrm{T};\mathrm{p}) + \mathrm{R}\,\mathrm{T}^{2}\,\mathrm{M}_1\,\mathrm{m_j}\left(\frac{\partial \phi}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

Hence,

$$\mathrm{C_{pl1}}\left(\mathrm{aq};\mathrm{m_j};\mathrm{T};\mathrm{p}\right) = \\ \mathrm{C}_{\mathrm{pl1}}^{*}(\ell;\mathrm{T};\mathrm{p}) + 2\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}\left(\frac{\partial \phi}{\partial \mathrm{T}}\right)_{\mathrm{p}} + \mathrm{R}\,\mathrm{T}^{2}\,\mathrm{M}_1\,\mathrm{m_j}\left(\frac{\partial^{2} \phi}{\partial \mathrm{T}^{2}}\right)_{\mathrm{p}}$$

Where

$$\mathrm{limit}\left(\mathrm{m_j} \to 0\right) \mathrm{C_{p1}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{C}_{\mathrm{pl1}}^{*}(\ell;\mathrm{T};\mathrm{p})$$

However,

$$\mathrm{C_p}(\mathrm{aq}) = \mathrm{n}_1\,\mathrm{C}_{\mathrm{p}_1}(\mathrm{aq}) + \mathrm{n_j}\,\mathrm{C_{pj}}\ (\mathrm{aq})$$

Hence, from equations (d) and (h),

$$\mathrm{C_p}\left(\mathrm{aq};\mathrm{m_j};\mathrm{T};\mathrm{p}\right) = \\ \mathrm{n}_1\left[\mathrm{C}_{\mathrm{pl}}^{*}(\ell;\mathrm{T};\mathrm{p}) + 2\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}\left(\frac{\partial \phi}{\partial \mathrm{T}}\right)_{\mathrm{p}}\right. \\ \left. + \mathrm{R}\,\mathrm{T}^{2}\,\mathrm{M}_1\,\mathrm{m_j}\left(\frac{\partial^{2} \phi}{\partial \mathrm{T}^{2}}\right)_{\mathrm{p}}\right] \\ + \mathrm{n_j}\left[\mathrm{C}_{\mathrm{pj}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) - 2\,\mathrm{R}\,\mathrm{T}\left(\frac{\partial \ln\left(\gamma_{\mathrm{j}}\right)}{\partial \mathrm{T}}\right)_{\mathrm{p}}\right. \\ \left. - \mathrm{R}\,\mathrm{T}^{2}\left(\frac{\partial^{2} \ln\left(\gamma_{\mathrm{j}}\right)}{\partial \mathrm{T}^{2}}\right)_{\mathrm{p}}\right]$$

We rearrange the latter equation to describe the isobaric heat capacity of a solution prepared using $1\ \mathrm{kg}$ of water [1].

$$\begin{aligned}&\mathrm{C_p\,(aq; m_j; w_1 = 1.0\ kg; T; p)} = \\ &\mathrm{(1/M_1)\ C^*_{pl}(\ell; T; p)} \\ &+ \mathrm{m_j}\left[\mathrm{C^\infty_{pj}(aq; T; p)} - 2\,\mathrm{R\,T}\left(\frac{\partial \ln(\gamma_j)}{\partial \mathrm{T}}\right)_\mathrm{p} - \mathrm{R\,T^2}\left(\frac{\partial^2 \ln(\gamma_j)}{\partial \mathrm{T^2}}\right)_\mathrm{p}\right. \\ &\left.+2\,\mathrm{R\,T}\left(\frac{\partial \phi}{\partial \mathrm{T}}\right)_\mathrm{p} + \mathrm{R\,T^2}\left(\frac{\partial^2 \phi}{\partial \mathrm{T^2}}\right)_\mathrm{p}\right]\end{aligned}$$

The term inside the [….] brackets is the apparent molar isobaric heat capacity for the solute. Thus,

$$\begin{aligned}\phi\,(C_{pj}) = C^\infty_{pj}(aq; T; p) - 2\,RT\left(\tfrac{\partial \ln(\gamma_j)}{\partial T}\right)_p \\ -RT^2\left(\tfrac{\partial^2 \ln(\gamma_j)}{\partial T^2}\right)_p \\ +2\,RT\left(\tfrac{\partial \phi}{\partial T}\right)_p + RT^2\left(\tfrac{\partial^2 \phi}{\partial T^2}\right)_p\end{aligned}$$

Hence,

$$\mathrm{C_p\,(aq; m_j; w_1 = 1.0\ kg; T; p)} = \mathrm{(1/M_1)\ C^*_{pl}(\ell; T; p)} + \mathrm{m_j}\,\phi\,(\mathrm{C_{pj}})$$

Then,

$$\mathrm{limit\,(m_j \to 0)}\,\phi\,(\mathrm{C_{pj}}) = \phi\,(\mathrm{C_{pj}})^\infty = \mathrm{C^\infty_{pj}(aq)}$$

Equation (m) shows that $\phi\,(\mathrm{C_{pj}})$ is a complicated property of a solution and that 'the devil is in the detail' [1]. A simplification in the algebra emerges if we define a set of J-properties which are excess properties [2,3]. Thus for a given solution prepared using $\mathrm{n_1}$ moles of water and n_j mole of solute j,

$$\mathrm{J(aq)} = \mathrm{n_1\,J_1(aq)} + \mathrm{n_j\,J_j(aq)}$$

where

$$J(aq) = C_p(aq) - C_p(aq; id)$$

$$\mathrm{J_1(aq)} = \mathrm{C_{p1}(aq)} - \mathrm{C^*_{pl1}(\ell)}$$

$$\mathrm{J_j(aq)} = \mathrm{C_{pj}(aq)} - \mathrm{C^\infty_{pj}(aq)}$$

$$\phi\,(\mathrm{J_j}) = \phi\,(\mathrm{C_{p_j}}) - \phi\,(\mathrm{C_{pj}})^\infty$$

But

$$\mathrm{C_p(aq)} - \mathrm{C_p(aq; id)} = \mathrm{n_j}\ [\phi\,(\mathrm{C_{pj}}) - \phi\,(\mathrm{C_{pj}})^\infty]$$

Then

$$\mathrm{J(aq)} = \mathrm{n_j}\,\phi\,(\mathrm{J_j})$$

An extensive literature reports the partial molar heat capacities of solutes in aqueous solution [2,3].

Further $\mathrm{C_{pj}}^\infty\mathrm{(aq)}$ for a range of related solutes can be analysed to yield group contributions [4-6]; e.g. at 298.15 K the contribution of a methyl group, $\mathrm{CH_3}$ to $\mathrm{C_{pj}}^\infty$ for an aliphatic solute is $178\ \mathrm{JK^{-1}\ mol^{-1}}$. Granted that $\mathrm{C_{pj}}^\infty\mathrm{(aq)}$ has been obtained for solute j and that the molar heat capacity of pure liquid j, $\mathrm{C^*_{pj}}(\ell)$ is known , the isobaric heat capacity of solution $\Delta_{s\,\ln}\mathrm{C^0_{pj}}$ is obtained [7].

$$\Delta_{s\,\ln}C^0_{pj} = C^\infty_{pj}(aq) - C^*_{pj}(\ell)$$

Footnotes

[1]

$$\mathrm{C_p\,(aq; m_j; w_1 = 1.0\ kg; T; p)} = \left[\mathrm{JK^{-1}\ kg^{-1}}\right]$$

$$\mathrm{(1/M_1)\ C^*_{pl}(\ell; T; p)} = \left[\mathrm{kgmol^{-1}}\right]^{-1}\ \left[\mathrm{JK^{-1}\ mol^{-1}}\right] = \left[\mathrm{JK^{-1}\ kg^{-1}}\right]$$

$$m_j\, C^{\infty}_{pj}(aq;T;p) = [molkg^{-1}]\ [JK^{-1}\ mol^{-1}] = [JK^{-1}\ kg^{-1}]$$

$$m_j\, 2\, R\, T \left(\frac{\partial \ln(\gamma_j)}{\partial T}\right)_p = [molkg^{-1}]\ [1]\ [Jmol^{-1}\ K^{-1}]\ [K]\,[K]^{-1} = [JK^{-1}\ kg^{-1}]$$

$$m_j\, R\, T^2 \left(\frac{\partial^2 \ln(\gamma_j)}{\partial T^2}\right)_p = [molkg^{-1}]\ [Jmol^{-1}\ K^{-1}]\ [K]^2\ [K^{-2} = [JK^{-1}\ kg^{-1}]$$

$$m_j\, 2\, R\, T \left(\frac{\partial \phi}{\partial T}\right)_p = [molkg^{-1}]\ [1]\ [Jmol^{-1}\ K^{-1}]\ [K]\ [K^{-1} = [JK^{-1}\ kg^{-1}]$$

$$m_j\, R\, T^2 \left(\frac{\partial^2 \phi}{\partial T^2}\right)_p = [molkg^{-1}]\ [Jmol^{-1}\ K^{-1}]\ [K]^2\,[K]^{-2} = [JK^{-1}\ kg^{-1}]$$

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1.15.2: Heat Capacities: Solutions: Solutes: Interaction Parameters

We describe an excess enthalpy $\mathrm{H^E}$ for a solution prepared using $1\ \mathrm{kg}$ of water and m_j moles of solute j (at fixed T and p) ion terms of solute-solute enthalpic interaction parameters.

$$\mathrm{H^E\,(aq;w_1=1\ kg)=h_{ij}\ \left(m_j/m^0\right)^2}$$

The corresponding excess isobaric heat capacity is defined by equation (b).

$$C_p^E\,(aq;w_1=1kg)=c_{pij}\ \left(m_j/m^0\right)^2$$

where

$$\mathrm{c_{pij}}=\left(\frac{\partial \mathrm{h_{ij}}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

Here $\mathrm{c_{pjj}}$ is a pairwise solute-solute interaction isobaric heat capacity [1]. From

$$\mathrm{H_1(aq)=H_1^*(\ell)-M_1\,h_{ij}\ \left(m_j/m^0\right)^2}$$

then,

$$\mathrm{C_{p1}(aq)=C^*_{pl^2}(\ell)-M_l\,c_{pjj}\ \left(m_j/m^0\right)^2}$$

From

$$\mathrm{H_j(aq)=H^\infty_{j'}(aq)+2\,h_{jj}\ \left(m^0\right)^{-2}\ m_j}$$

then,

$$\mathrm{C_{pj}(aq)=C^\infty_{pj}(aq)+2\,c_{pjj}\ \left(m^0\right)^{-2}\ m_j}$$

Footnote

[1] For a solution prepared using $1\ \mathrm{kg}$ of water and m_j moles of solute (at fixed T and p)

$$\mathrm{C_p\,(aq;w_1=1\ kg)=(1/M_1)\ C_{p1}(aq)+m_j\,C_{pj}(aq)}$$

Hence

$$\mathrm{C_p\,(aq;w_1=1\ kg)=(1/M_1)\ \left[C^*_{pl}(\ell)-M_1\,c_{pjj}\ \left(m_j/m^0\right)^2\right]}$$
$$\mathrm{+m_j\ \left[C^\infty_{pj}(aq)+2\,c_{pjj}\ \left(m^0\right)^{-2}\ m_j\right]}$$

Then,

$$\mathrm{C_p\,(aq;w_1=1\ kg)=(1/M_1)\ C^*_{p1}(\ell)+m_j\,C^\infty_{pj}(aq)+c_{pji}\ \left(m_j/m^0\right)^2}$$

Since,

$$\mathrm{C_p\,(aq;id;w_1=1\ kg)=(1/M_1)\ C^*_{pl1}(aq)+m_j\,C^\infty_{pj}(aq)}$$
$$\mathrm{C^E_p\,(aq;w_1=1\ kg)=c_{pjj}\ \left(m_j/m^0\right)^2}$$

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1.15.3: Heat Capacities: Isobaric: Solutions: Unit Volume

A given aqueous solution was prepared using n_1 moles of water(ℓ) and n_j moles of solute j. Then,

$$\mathrm{C_p(aq) = n_1\, C^*_{pl}(\ell) + n_j\, \phi\,(C_{pj})}$$

For the solution, by definition, the isobaric heat capacity per unit volume, (or heat capacitance)

$$\sigma(\mathrm{aq}) = \mathrm{C_p(aq)/V(aq)}$$

Similarly for the solvent at the same temperature and pressure,

$$\sigma^*_1(\ell) = \mathrm{C^*_{p1}}(\ell)/\mathrm{V}^*_1(\ell)$$

With reference to equations (b) and (c), the four experimentally determined quantities are $\sigma(\mathrm{aq}), \sigma^*_1(\mathrm{aq}), \rho(\mathrm{aq})$ and $\rho^*_1(\ell)$. The latter two quantities are the densities of the solution and solvent respectively.

Hence $\sigma(\mathrm{aq})$ is related to the concentration of the solution, c_j [1,2].

$$\sigma(\mathrm{aq}) = \sigma^*_1(\ell) + [\phi\,(\mathrm{C_{pj}}) - \phi\,(\mathrm{V_j})\ \sigma^*_1(\ell)]\ \mathrm{c_j}$$

The latter equation relates $\sigma(\mathrm{aq})$ to the property for the pure solvent, $\sigma^*_1(\ell)$ and to the concentration of solute, $\mathrm{c_j}$. Equation (d) relates $\phi\,(\mathrm{C_{pj}})$ to the measured quantities $\sigma(\mathrm{aq})$ and $\sigma^*_1(\ell)$ together with the apparent molar volume $\phi\,(\mathrm{V_j})$. Thus $\sigma(\mathrm{aq})$ and $\phi\,(\mathrm{V_j})$ for a given solution yields together with $\sigma^*_1(\ell)$, the apparent molar isobaric heat capacity of the solute, $\phi\,(\mathrm{C_{pj}})$. In cases where the composition of the solution is expressed using molalities, equation (e) is the equation for $\phi\,(\mathrm{C_{pj}})$ [3,4].

$$\begin{aligned}\phi\,(\mathrm{C_{pj}}) =& [\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho^*_1(\ell)]^{-1}\ [\rho^*_1(\ell)\,\sigma(\mathrm{aq}) - \rho(\mathrm{aq})\,\sigma^*_1(\ell)] \\ &+ \mathrm{M_j}\,\sigma(\mathrm{aq})/\rho(\mathrm{aq})\end{aligned}$$

Footnotes

[1] From equations (a) and (b),

$$\sigma(\mathrm{aq}) = [\mathrm{n_1/V(aq)}]\ [\mathrm{V}^*_1(\ell)/\mathrm{V}^*_1(\ell)]\ \mathrm{C^*_{p1}}(\ell) + [\mathrm{n_j/V(aq)}]\ \phi\,(\mathrm{C_{pj}})$$

The term $[\mathrm{V}^*_1(\ell)/\mathrm{v}^*_1(\ell)]$ has been introduced with the definition of $\sigma^*_1(\ell)$ in mind.

But,

$$\mathrm{V(aq) = n_1\, V^*_1}(\ell) + \mathrm{n_j}\,\phi\,(\mathrm{V_j})$$

or,

$$\mathrm{n_l\, V^*_1}(\ell) = \mathrm{V(aq)} - \mathrm{n_j}\,\phi\,(\mathrm{V_j})$$

Further concentration, $\mathrm{c_j = n_j/V}$ Then,

$$\sigma(\mathrm{aq}) = [\mathrm{V(aq)} - \mathrm{n_j}\,\phi\,(\mathrm{V_j})]\ [\mathrm{V(aq)}]^{-1}\,\sigma^*_1(\ell) + \mathrm{c_j}\,\phi\,(\mathrm{C_{pj}})$$

Hence,

$$\sigma(\mathrm{aq}) = \sigma^*_1(\ell)\ [1 - \mathrm{c_j}\,(\mathrm{V_j})] + \mathrm{c_j}\,\phi\,(\mathrm{C_{pj}})$$

or

$$\sigma(\mathrm{aq}) = \sigma^*_1(\ell) + [\phi\,(\mathrm{C_{pj}}) - \phi\,(\mathrm{V_j})\ \sigma^*_1(\ell)]\ \mathrm{c_j}$$

[2]

$$\begin{aligned}\phi\,(\mathrm{C_{pj}})\ \mathrm{c_j} &= \left[\mathrm{JK^{-1}\ mol^{-1}}\right]\left[\frac{\mathrm{mol}}{\mathrm{m^3}}\right] = \left[\mathrm{JK^{-1}\ m^{-3}}\right] \\ \phi\,(\mathrm{V_j})\ \sigma^*_1(\ell)\,\mathrm{c_j} &= \left[\mathrm{m^3\ mol^{-1}}\right]\left[\mathrm{JK^{-1}\ m^{-3}}\right]\left[\mathrm{molm^{-3}}\right] = \left[\mathrm{JK^{-1}\ m^{-3}}\right]\end{aligned}$$

[3] From [1],

$$\mathrm{V(aq)} = \left[\mathrm{n_1\,V_1^*}(\ell)\,\sigma_1^*(\ell)/\sigma(\mathrm{aq})\right] + \mathrm{n_j}\,\phi\left(\mathrm{C_{pj}}\right)/\sigma(\mathrm{aq})$$

But,

$$\mathrm{V(aq)} = \left(\mathrm{n_1\,M_1} + \mathrm{n_j\,M_j}\right)/\rho(\mathrm{aq})$$

Then,

$$\frac{\mathrm{n_1\,M_1} + \mathrm{n_j\,M_j}}{\rho(\mathrm{aq})} = \left[\mathrm{n_1\,V_1^*}(\ell)\,\sigma_1^*(\ell)/\sigma(\mathrm{aq})\right] + \mathrm{n_j}\,\phi\left(\mathrm{C_{pj}}\right)/\sigma(\mathrm{aq})$$

or (dividing by $\mathrm{n_j}$),

$$\left[\frac{\mathrm{n_1\,M_1}}{\rho(\mathrm{aq})\,\mathrm{n_j}}\right] + \left[\frac{\mathrm{n_j\,M_j}}{\mathrm{n_j}\,\rho(\mathrm{aq})}\right] = \left[\frac{\mathrm{n_1\,V_1^*}(\ell)\,\sigma_1^*(\ell)}{\mathrm{n_j}\,\sigma(\mathrm{aq})}\right] + \frac{\phi\left(\mathrm{C_{pj}}\right)}{\sigma(\mathrm{aq})}$$

But molality $\mathrm{m_j} = \mathrm{n_j}/\mathrm{n_1\,M_1} = \mathrm{n_j}/\mathrm{n_1\,V_1^*}(\ell)\,\rho_1^*(\ell)$ Then,

$$\left[\frac{1}{\rho(\mathrm{aq})\,\mathrm{m_j}}\right] - \left[\frac{\sigma_1^*(\ell)}{\rho_1^*(\ell)\,\mathrm{m_j}\,\sigma(\mathrm{aq})}\right] + \frac{\mathrm{M_j}}{\rho(\mathrm{aq})} = \frac{\phi\left(\mathrm{C_{pj}}\right)}{\sigma(\mathrm{aq})}$$

As an equation for $\phi\left(\mathrm{C_{pj}}\right)$;

$$\phi\left(\mathrm{C_{pj}}\right) = \frac{\sigma(\mathrm{aq})}{\rho(\mathrm{aq})\,\mathrm{m_j}} - \frac{\sigma_1^*(\ell)}{\rho_1^*(\ell)\,\mathrm{m_j}} + \frac{\mathrm{M_j}\,\sigma(\mathrm{aq})}{\rho(\mathrm{aq})}$$

Hence

$$\phi\left(\mathrm{C_{pj}}\right) = \left[\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_1^*(\ell)\right]^{-1}\left[\rho_1^*(\ell)\,\sigma(\mathrm{aq}) - \rho(\mathrm{aq})\,\sigma_1^*(\ell)\right] + \mathrm{M_j}\,\sigma(\mathrm{aq})/\rho(\mathrm{aq})$$

[4]

$$\left[\mathrm{m_j}\,\rho(\mathrm{aq})\,\rho_1^*(\ell)\right]^{-1}\left[\rho_1^*(\ell)\,\sigma(\mathrm{aq}) - \rho(\mathrm{aq})\,\sigma_1^*(\ell)\right] = \left[\frac{\mathrm{kg}}{\mathrm{mol}}\right]\left[\frac{\mathrm{m^3}}{\mathrm{kg}}\right]\left[\frac{\mathrm{m^3}}{\mathrm{kg}}\right]\left[\frac{\mathrm{kg}}{\mathrm{m^3}}\right]\left[\mathrm{JK^{-1}\ m^{-3}}\right] = \left[\mathrm{JK^{-1}\ mol^{-1}}\right]$$

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1.15.4: Heat Capacities: Isobaric: Salt Solutions

The excess enthalpy H^E of an aqueous salt solution prepared using $1\ kg$ of water and m_j moles of a 1:1 salt is related to m_j using the DHLL. Because ${C_p}^E$ is the isobaric temperature dependence of H^E, then ${C_p}^E$ for this aqueous solution is given by equation (a) [1].

$$C_p^E\,(aq; w_1 = 1\ kg) = -(4/3)\,R\,m_j^{(3/2)}\ \left(m^0\right)^{-1/2}\left[2\,T\,S_H + T^2\ (\partial S_H/\partial T)_p\right]$$

$$S_{Cp_p} = 2\,T\,S_H + T^2\ (\partial S_H/\partial T)$$

S_{Cp} is the DHLL factor in the equation for the isobaric heat capacity.

$$C_p^E\,(aq; w_1 = 1\ kg) = -(4/3)\,R\,S_{Cp}\,m_j^{(3/2)}\ \left(m^0\right)^{-1/2}$$

Using equation (c) [2],

$$\phi\,(J_j) = -(4/3)\,R\,S_{Cp_p}\ \left(m_j/m^0\right)^{1/2}$$

We could perhaps have anticipated that according to DHLL, Extra close brace or missing open brace is a linear function of $(m_j)^{1/2}$. An extensive literature describes the limiting partial molar isobaric heat capacities of ions in aqueous solution. One of the earliest investigations of the isobaric heat capacities of salt solutions was made by Randall and Ramage[3] and later by Randall and Taylor [4]. The groups lead by Hepler [5,6] and by Desnoyers [7] have made significant contributions in this area. However no agreement has been reached on a scale of absolute values. Hepler reported relative estimates based on $C_p^\infty\,(H^+; aq; 298\ K)$ equal to zero. Perhaps most attention has been directed at salts formed by alkylammonium cation [8,9] and hydrophobic anions; e.g. amino acids [10], phenylcarboxylates, t-butylcarboxlates[11] and cryptates[12]. Data [7] for $R_4\ N^+Br^-(aq)$ show that $C_{pj}^\infty(aq)$ increases with increase in hydrophobic character of the R-group. French and Criss argue [13] in favour of a scale which sets $C_p^\infty\,(Br^-; aq)$ at –68 $JK^{-1}\ mol^{-1}$. An attempt[14] has identified the various contributions to $C_p^\infty(\ ion;\ aq\ )$. Certainly trends in $C_p^\infty(\ ion;\ aq\ )$ point to characteristic features associated with the properties of ions in aqueous solution. Nevertheless, interpretation is not straightforward [14].

Footnotes

[1]

$$S_{Cp} = 2\,T\,S_H + T^2\ (\partial S_H/\partial T)_p = [1]\,[K]\ \left[K^{-1}\right] + [K]^2\ \left[K^{-1}\right]\ [K]^{-1} = [1]$$

[2]

$$\phi\,(J_j) = [1]\ \left[JK^{-1}\ mol^{-1}\right]\ [1]\,[1] = \left[JK^{-1}\ mol^{-1}\right]$$

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1.15.5: Heat Capacities: Isochoric: Liquid Mixtures: Ideal

For an ideal binary liquid mixture the molar isobaric heat capacity is given by the mole fraction weighted sum of the isobaric heat capacities of the pure liquid components.

$$\mathrm{C_{pm}(mix;id)} = \mathrm{x_1\,C^*_{p1}}(\ell) + \mathrm{x_2\,C^*_{p2}}(\ell)$$

Both $\mathrm{C^*_{p1}}(\ell)$ and $\mathrm{C^*_{p2}}(\ell)$ can be measured so that $\mathrm{C_{pm}(mix;id)}$ can be calculated for a given mixture as a function of mole fraction composition. Further

$$\Delta_{\mathrm{mix}}\mathrm{C_p(id)} = 0$$

The isochoric heat capacity of the corresponding ideal mixture is related to the isobaric heat capacity using equation (c) [1].

$$\mathrm{C_{V_m}(\ mix\ ;id)} = \mathrm{C_{pm}(\ mix\ ;id)} - \frac{\mathrm{T\ [E_{pm}(\ mix;id)]^2}}{\mathrm{K_{Tm}(\ mix\ ;id)}}$$

Equations (a) and (c) provide an equation for $\mathrm{C_{Vm}(mix;id)}$ in terms of the isochoric heat capacities of the pure liquid components.

$$\begin{aligned}&\mathrm{C_{V_m}(mix;id)} = \\ &\mathrm{x_1}\left[\mathrm{C^*_{V1}}(\ell) + \frac{\mathrm{T\ \left[E^*_{p1}}(\ell)\right]^2}{\mathrm{K^*_{T1}}(\ell)}\right] + \mathrm{x_2}\left[\mathrm{C^*_{V2}}(\ell) + \frac{\mathrm{T\ \left[E^*_{p2}}(\ell)\right]^2}{\mathrm{K^*_{T2}}(\ell)}\right] \\ &- \frac{\mathrm{T\ [E_{pm}(mix;id)]^2}}{\mathrm{K_{Tm}(mix;id)}}\end{aligned}$$

In terms of forming an ideal binary liquid mixture from two pure components,

$$\begin{aligned}\Delta_{\mathrm{mix}}\mathrm{C_{V_m}(id)} = \mathrm{x_1}&\left[\frac{\mathrm{T\ \left[E^*_{p1}}(\ell)\right]^2}{\mathrm{K^*_{T1}}(\ell)}\right] + \mathrm{x_2}\left[\frac{\mathrm{T\ \left[E^*_{p2}}(\ell)\right]^2}{\mathrm{K^*_{T2}}(\ell)}\right] \\ &- \frac{\mathrm{T\ [E_{pm}(mix;id)]^2}}{\mathrm{K_{Tm}(mix;id)}}\end{aligned}$$

The equations become more complicated as we switch conditions from the intensive variables, T and p, to extensive variables such as entropy and volume. The equations become even more complicated when we turn to a description of real mixtures.

Footnote

[1] Consider a closed system subjected to a change in temperature, the system remaining at equilibrium where the affinity for spontaneous change is zero. Then

$$\mathrm{C_p(A=0)} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p,A=0}} \quad \text{and} \quad \mathrm{C_V(A=0)} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V,A=0}}$$

In the following we drop the condition '$\mathrm{A=0}$' and take it as implicit in the following analysis. [A similar set of equations can be written for the condition 'at fixed ξ'.] Then $\mathrm{C_p - C_V} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p}} - \left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$ but by definition, $\mathrm{H = U + p\,V}$ Then

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial H}{\partial T}\right)_v + V\left(\frac{\partial p}{\partial T}\right)_v$$

Using a calculus operation, $\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{v}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p}} + \left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T}}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{v}}$ Then,

$$\mathrm{C_p - C_V} = \left[\mathrm{V} - \left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T}}\right]\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

By definition $\mathrm{H = G + T\,S}$; then

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right)_{\mathrm{T}} + \mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

A Maxwell equation requires that $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$ Then, $\left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \mathrm{V} - \mathrm{T}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$ Hence,

$$\mathrm{C_p - C_V = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V}$$

A calculus operation requires that $\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$ Then

$$C_p - C_V = -T\left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2 \left[\left(\frac{\partial V}{\partial p}\right)_T\right]^{-1}$$

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SECTION OVERVIEW

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Topic hierarchy

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1.16.2: Ionic Mobilities: Aqueous Solutions

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1.16.4: Ion-Water Interactions

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1.16.1: Ion Association

The term ‘ strong electrolyte’ has a long and honourable history in the development of an understanding of the properties of salt solutions. This term describes salt solutions where each ion contributes to the properties **almost** independently of all other ions in a given solution. The word ‘almost’ signals that the properties of a given salt solution are determined in part by charge –charge interactions between ions through the solvent separating ions in solution. Otherwise the ions can be regarded as free. Such is the case for aqueous salt solutions at ambient temperatures and pressures prepared using 1:1 salts such as Na^+Cl^-, $Et_4N^+Br^-$ …

However with decrease in relative permittivity of the solvent, the properties of salt solutions indicate that not all the ions can be regarded as free; a fraction of the ions are associated. For dilute salts solutions in apolar solvents such as propanone a fraction of the salt is described as being present as ion pairs formed by association of cations and anions. With further decrease in the permittivity of the solvent higher clusters are envisaged; e.g. triple ions, quadruple ions…. Here we concentrate attention on ion pair formation building on the model proposed by N. Bjerrum [1,2].

The analysis identifies a given j ion in a salt solution as the reference ion such that at distant r from this ion the electric potential equals ψ_j whereby the potential energy of ion i with charge number z_i equals $z_i\ e\ \psi_j. The solvent is a structureless continuum and each ion is a hard non-polarisable sphere characterised by its charge, \(z_j\ e$, and radius r_j.

If the bulk number concentration of i ions is p_i, the average local concentration of i ions' p_i is given by equation (a) [3].

$$p_i' = n_i\ \exp\left(-z_i\ e\ \psi_j / k\ T\right)$$

The number of i-ions, dn_i in a shell thickness dr distance r from the reference j ion is given by equation (b) [4].

$$p_j = n_i\ \exp\left(-z_i\ e\ \psi_j / k\ T\right)\ 4\ \pi\ r^2\ dr$$

At small r, the electric potential arising from the j ion is dominant. Hence [5],

$$\psi_j = \frac{z_j\ e}{4\ \pi\ \varepsilon_0\ \varepsilon_r\ r}$$

Hence,

$$dn_i = p_i\ \exp\left(-\frac{z_i\ e}{k\ T}\ \frac{z_j\ e}{4\ \pi\ \varepsilon_0\ \varepsilon_r\ r}\right)\ 4\ \pi\ r^2\ dr$$

Or [6],

$$dn_i = p_i\ \exp\left(-\frac{z_i\ z_j\ e^2}{4\ \pi\ k\ T\ \varepsilon_0\ \varepsilon_r\ r}\right)\ 4\ \pi\ r^2\ dr$$

Using equation (e), the number of ions in a shell, thickness dr and distance r from the j ion, at temperature T in a solvent having relative permittivity ε_r is obtained for ions with charge numbers z_i and z_j.

For two ions having the same sign dn_i increases with increase in r, a pattern intuitively predicted. However for ions of opposite sign an interesting pattern emerges in which dn_i decreases with increase in r, passes through a minimum and then increases. In other words there exists a distance q at which there is a minimum in the probability of finding a counterion. Thus [7]

$$q = \frac{|z_i\ z_j|\ e^2}{8\ \pi\ \varepsilon_0\ \varepsilon_r\ k\ T}$$

For a given salt, q increases with decrease in ε_r at fixed T. Bjerrum suggested that the term ‘ion pair’ describes two counter ions where their distance apart is less than q [8]. In other words the proportion of a given salt in solution in the form of ions pairs increases with decrease in ε_r. The interplay between solvent permittivity and ion size a_j as determined by the sum of cation and anion radii is important. For a fixed a_j, the fraction of ions present as ion pairs increases with decrease in relative permittivity of the solvent. Thus high ε_r favours description of a salt as present as only ‘free’ cations and anions. The properties of such a real solutions might therefore be described using the Debye-Huckel Limiting Law. By way of contrast as ε_r decreases the extent of ion pair formation increases with decrease in ion size [9].

Ion Association

The fraction of salt in solution θ in the form of ion pairs is given by the integral of equation (e) within the limits a and q where a is the distance of closest approach of cation and anion. Thus

$$\theta = 4\,\pi\,p_i \int_a^q \exp\left(-\frac{z_+\,z_-\,e^2}{4\,\pi\,\varepsilon_0\,\varepsilon_r\,k\,T\,r}\right) r^2\,dr$$

Hence [10], for a solution where the concentration of salt c_j expressed using the unit, moldm^{-3}, θ is given by equation (h).

$$\theta = \frac{4\,\pi\,N}{10^3}\left(\frac{|\mathrm{z_+\,z_-\,e^2}|}{4\,\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{k\,T}}\right)^3 \mathrm{Q(b)}$$

where

$$Q(b) = \int_2^b x^{-4}\,e^x\,dx$$

with

$$\mathrm{b} = \frac{|\mathrm{z_+\,z_-}|\;\mathrm{e}^2}{4\,\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{k\,T\,a}}$$

and

$$\mathrm{x} = -\frac{\mathrm{z_+\,z_-\,e^2}}{4\,\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{k\,T\,r}}$$

The integral $\mathrm{Q(b)}$ has been tabulated as a function of b [1,10]. According to equation (h), θ increases with increase in b; i.e. with increase in a and decrease in ε_r.

Ion Pair Association Constants

The analysis leading to equation (h) is based on concentrations of salts in solution. Therefore the equilibrium between ions and ion pairs is described using concentration units. Here we consider the case of a 1:1 salt (e.g $\mathrm{Na^+Cl^-}$) in the form of the following equilibrium describing the dissociation of ion pairs. [A common convention in this subject is to consider 'dissociation'.] For a 1:1 salt j in solution the chemical potential $\mu_j(s\,\mathrm{ln})$ is given by equation (l).

$$\mu_\mathrm{j}(\mathrm{s\,ln}) = \mu_\mathrm{j}^0(\,\mathrm{s\,ln}) + 2\,\mathrm{R\,T}\,\ln\left(\mathrm{c_j\,y_\pm/c_r}\right)$$

The mean ionic activity coefficient (concentration scale) is defined by equation (m)

$$\mathrm{limit}\,(c_j \to 0)\,y_\pm = 1.0\;\mathrm{at\;all\;T\;and}\;p$$

The thermodynamic properties of the neutral (dipolar) ion pair are treated as ideal. Then,

$$\mu_\mathrm{ip}(\mathrm{s\,ln}) = \mu_\mathrm{ip}^0(\,\mathrm{s\,ln}) + \mathrm{R\,T}\,\ln\left(\mathrm{c_{ip}/c_r}\right)$$

The equilibrium between 'free' ions (i.e. salt j) and ion pairs is described by the following equation.

$$\mathrm{M^+X^-(s\,ln)} \Longleftrightarrow \mathrm{M^+(s\,ln) + X^-(s\,ln)}$$

Then,

$$\mu_{ip}(s\,\mathrm{ln}) = \mu_j(s\,\mathrm{ln})$$

Hence the ion pair dissociation constants $\mathrm{K_D}$ is given by equation (q).

$$\Delta_\mathrm{diss}\,G^0 = -RT\,\ln\left(K_D\right)$$

where

$$\Delta_\mathrm{diss}\,G^0 = \mu_j^0(s\,\mathrm{ln}) - \mu_\mathrm{ip}^0(\,\mathrm{s\,ln})$$

Hence,

$$K_D = \frac{(c_j\, y_{\pm}/c_r)^2}{(c_{ip}/c_r)}$$

But $\mathrm{c_j} = \theta\, \mathrm{c_s}$ and $\mathrm{c_{ip}} = (1-\theta)\, \mathrm{c_s}$ where $\mathrm{c_s}$ is the total concentration of salt $\mathrm{M^+X^-}$. Then,

$$\mathrm{K_D} = \frac{\theta^2\, \mathrm{y_{\pm}^2\, c_s}}{(1-\theta)\, \mathrm{c_r}}$$

$\mathrm{K_D}$ is dimensionless. The long-established convention in this subject defines a quantity $\mathrm{K_D'}$. Thus

$$\mathrm{K_D'} = \frac{\theta^2\, \mathrm{y_{\pm}^2\, c_s}}{(1-\theta)}$$

For very dilute solutions, the assumption is made that $\theta = 1$ and $\mathrm{y_{\pm}} = 1$. Hence using equation (h),

$$\frac{1}{\mathrm{K_D'}} \cong \frac{1-\theta}{\mathrm{C_S}}$$

$$\theta = \frac{4\,\pi\, N}{10^3} \left(\frac{|\mathrm{z_+\, z_-}|\ \mathrm{e}^2}{4\,\pi\, \varepsilon_0\, \varepsilon_\mathrm{r}\, \mathrm{k\, T}} \right)^3 \mathrm{Q(b)}$$

Conductivities of Salt Solutions

The molar conductances of salt solutions at fixed T and p can be precisely measured. To a first approximation the molar conductance of a given solution offers a method of counting the number of free ions. For salt solutions in solvents of low permittivity the molar conductance offers a direct method for assessing the fraction of salt present as free ions and hence the fraction present as ion pairs. Hence electrical conductivities of salt solutions in solvents of low relative permittivity have been extensively studied in order to probe the phenomenon of ion pair formation.

The classic study was reported [10] by Fuoss and Kraus in 1933 who studied the electrical conductivities of tetra-iso-amylammonium nitrate in dioxan + water mixtures [11] at $298.15\ \mathrm{K}$ over the range $2.2 \leq \varepsilon_\mathrm{r} \leq 78.6$. The dependence of measured dissociation constants followed the pattern required by Bjerrum's theory. Following the publication of the study by Fuoss and Kraus [10], many papers were published confirming the general validity of the Bjerrum ion-pair model. We note below a few examples of these studies which lead in turn to developments of the theory. For example in solvents of very low relative pemitivities triple ions are formed of the ++- and +-- type [12,13]. Many experimental techniques have been used to support the Bjerrum model; e.g. cryoscopic studies [14], electric permittivities of solutions [15,16] and Wien effects [17].

Following the Bjerrum model, other models were suggested and developed. Denison and Ramsey [18] suggested that the term 'ion pair' describes ions in contact, all other ions being free. Sadek and Fuoss [19] proposed that association of free ions to form contact ion ion pairs involved formation of solvent separated ion pairs, although they later withdrew the proposal[20]. Gilkerson [21] modified equations describing ion-pair formation to include parameters describing ion-solvent interaction. In 1957 Fuoss [22] restricted the definition of the term 'ion pair' to ions in contact. The dipolar nature of an ion pair was confirmed by dielectric relaxation studies [23,24]. In the development of theories of ion pair formation Hammett notes the models of ion pair formation which involve charged spheres in a continuous dielectric may only be relevant under especially favourable circumstances [25].

General Comments

The initial proposal by Bjerrum concerning ion pair formation has had an enormous impact in many branches of chemistry including mechanistic organic chemistry [26,27]. Spectroscopic studies identified ion-pairs in solution using charge transfer to solvent spectra [28]. Electron spin resonance identified the presence of ion pairs in solution. Particularly interesting are those solutions where the counterion hops between two sites in an organic radical anion [29].

Returning to the context of thermodynamics, the Bjerrum model of ion association has been extended to descriptions of partial molar volumes [30], apparent molar heat capacities and compressibilities of salts in non-aqueous solutions including cyanomethane [31].

Nevertheless the debate concerning ion association in solution has continued particularly with the development of statistical thermodynamic treatments of salt solutions. Grunwald [32] comments on the debate. To some extent the question arises as to the extent to which formation of ions pairs is either assumed from the outset or emerges from a given theoretical model for a salt solution.

Footnotes

[1] N. Bjerrum, K. Danske Vidensk Selskab, 1926,**7**, No. 9.

[2] For more recent accounts see—

a. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd ed. Revised,1965, chapter 14.
b. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 2nd. edition, revised and enlarged, 1950, section 3-7.
c. S. Glasstone, An Introduction to Electrochemistry, D. Van Nostrand, New York, 1942.
d. J. O'M. Bockris and A. J K. N. Reddy, Modern Electrochemistry: Ionics, Plenum Press, New York, 2nd. edn.,1998,chapter 3.

[3]

$$\frac{z_i\, e\, \psi_j}{k\, T} = \frac{[1]\,[C]\,[V]}{[JK^{-1}]\,[K]} = \frac{[As]\;[JAs^{-1}]}{[J]} = [1]$$
$$p_i = [m^{-3}] \quad p_i' = [m^{-3}]$$

[4]

$$p_i\, \exp\left(-z_i\, e\, \Psi_j / k\, T\right)\, 4\,\pi\, r^2\, dr = \frac{1}{[\,m^3]}\,[1]\,[1]\;[m^3] = [1]$$

[5]

$$\psi_j = \frac{[1]\,[C]}{[1]\,[1]\;[Fm^{-1}]\;[1]\,[m]} = \frac{[As]}{[AsV^{-1}]} = [V]$$

[6]

$$\left(-\frac{z_i\, z_j\, e^2}{4\,\pi\, k\, T\, \varepsilon_0\, \varepsilon_r\, r}\right)$$
$$= \frac{[1]\,[1]\,[C]^2}{[1]\,[1]\;[JK^{-1}]\;[K]\;[Fm^{-1}]\;[1]\,[m]} = \frac{[As]^2}{[\,J]\,[F]}$$
$$= \frac{[As]^2}{[\,J]\;[AsAsJ^{-1}]} = [1]$$

Hence, $p_j = [molm^{-3}]\;[1]\,[1]\,[1]\;[m^2]\;[m] = [1]$

[7]

$$q = \frac{[1]\,[1]\,[C]^2}{[1]\,[1]\;[Fm^{-1}]\;[1]\;[JK^{-1}]\;[K]} = \frac{[A\,s]^2}{[\,A^2\;s^2\;J^{-1}\;m^{-1}]\;[J]} = [m]$$

[8] Distance q corresponds to the distance where $\frac{|z_i\, z_j|\, e^2}{4\,\pi\,\varepsilon_0\,\varepsilon_r\, q} = 2\,k\,T$

[9] We stress the distinction between association of cation M^+ and anion X^- to form an ion pair and association in solution of H^+ and CH_3COO^- ions to form undissociated ethanoic acid. In the later case the cohesion is discussed in quantum mechanical terms.

[10] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc.,1933,**55**,1019.

[11] The liquid mixture dioxan + water is notable for being completely miscible and ambient T and p, the relative permitivities having a remarkable range. No other water + organic liquid offers such a range.

[12] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc.,1933,**55**,2387.

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1.16.2: Ionic Mobilities: Aqueous Solutions

A classic subject in physical chemistry concerns the electric conductivities of salt solutions, most interest being centred on the aqueous salt solutions. Although the electric conductivities of these systems, transport properties, do not come under the heading 'thermodynamic properties', these conductivities have played a major part in the task of understanding the thermodynamic properties of salt solutions.

Generally however interest in the electric conductivities of salt solutions has waned as spectroscopic properties in all its form have moved to a dominant position in physical chemistry. Nevertheless the contributions made by research into the electric properties of salt solutions have been and remain enormously important.

Conductivities

At this point there is merit in commenting on the technique, mass spectrometry. In this important experimental technique, ions are produced in an ion source and then subjected to an electric field gradient, where (usually) cations are **accelerated**. The ions pass through a magnetic field, the path of a given ion depending on the charge and mass of the ion.

Descriptions of the electrical conductivities of salt solutions start out from a quite different basis. To understand the point we consider a reasonably concentrated aqueous solution of sodium chloride; i.e. $0.1\ \mathrm{moldm^{-3}} \equiv 0.1\ \mathrm{mol}$ salt in water, mass $1\ \mathrm{kg} \equiv 0.1\ \mathrm{mol}$ salt in $(1.0/0.018)\ \mathrm{mol\ water} \equiv 0.1\ \mathrm{molNa^{+}\ ions} + 0.1\ \mathrm{molCl^{-}\ ions} + 55.6\ \mathrm{mol\ water}(\ell)$. In other words, for every sodium ion there are 556 molecules of water in this aqueous solution. The contrast with the mass spectrometer experiment could not be more dramatic. Further in conventional experiments studying the electric conductivities of salt solutions, the effect of a modest electric potential gradient is simply to bias the otherwise Brownian motion of the ion in a direction depending on the sign of the charge on a given ion. As each ion makes its way through the solution it is jostled and impeded by the large number of solvent molecules. Nevertheless in theoretical treatments of the electric conductivities of salt solutions the theory envisages a slow direct progress through the solution, in the case of, for example, a cation down the electric potential gradient. The key experimental fact is that the electric properties of salt solutions at low electric currents and low electric potential gradients obey the phenomenological law, Ohm's Law. Deviations from this law are observed for example at high electrical field gradients; e.g. Wien Effects.

Molar Conductivities

The key term in the context of the electric conductivities of a salt solution, concentration of salt c_j is the molar conductivity Λ defined by equation (a) where κ is the electrolytic conductivity [1,2].

$$\Lambda = \kappa/\mathrm{c}_j$$

For a salt solution prepared using a 1:1 salt , the molar conductivity can be expressed as the sum of ionic conductivities , λ_+ and λ_-. Thus

$$\Lambda = \lambda_+ + \lambda_-$$

Using equation (a), the electrolytic conductivity κ is related to the ionic conductivities using equation (c)

$$\kappa = \mathrm{c_j}\ (\lambda_+ + \lambda_-)$$

The electric mobility of a given ion, u_j is related to the mobility v_j using equation (d) [3].

$$\mathrm{u_j} = \mathrm{v_j}/\mathrm{E}$$

Footnotes

[1]

$$\begin{aligned}\kappa &= (\text{ electric current density}) \ / \ (\text{electric field strength }) \\ &= [\mathrm{j}]/[\mathrm{E}] \\ &= \left[\mathrm{Am^{-2}}\right] / \left[\mathrm{Vm^{-1}}\right] = \left[\mathrm{Sm^{-1}}\right]\end{aligned}$$

[2] $\Lambda = \left[\mathrm{Sm^{-1}}\right] / \left[\mathrm{molm^{-3}}\right] = \left[\mathrm{Sm^2\ mol^{-1}}\right]$

[3] $\mathrm{u_j} = \left[\mathrm{ms^{-1}}\right] / \left[\mathrm{Vm^{-1}}\right] = \left[\mathrm{m^2\ s^{-1}\ V^{-1}}\right]$

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1.16.3: Ionic Strength: Ional Concentration

The ionic strength of a salt solution I containing i-ionic substances is defined by equation (a); m_j is the molality of ionic substance-j, charge number z_j [1].

$$\mathrm{I} = (1/2) \sum_{\mathrm{j=i}}^{\mathrm{j=i}} \mathrm{m_j}\, \mathrm{z_j^2}$$

The sum is taken over all i-ionic substances in the solution. The situation is slightly complicated by the fact some authors use the term 'ionic strength' where the concentration c_j (expressed using the unit, $\mathrm{moldm^{-3}}$) replaces m_j. The substitution is reasonably satisfactory for dilute salt solutions at ambient T and p where the mass of water, volume $1\ \mathrm{dm^3}$, is approx. $1\ \mathrm{kg}$.

The ional concentration of a salt solution Γ is defined by equation (b) where c_j is expressed using the unit, $\mathrm{moldm^{-3}}$ [2].

$$\Gamma = \sum_{j=i}^{j=i} c_j\, z_j^2$$

Footnotes

[1] An aqueous solution contains $\mathrm{K_2SO_4}$ $(0.1\ \mathrm{mol})$ in $1\ \mathrm{kg}$ of water(ℓ).

$\mathrm{m}\,(\mathrm{K_2SO_4}) = 0.1\ \mathrm{mol\ kg^{-1}}; \mathrm{m}\,(\mathrm{K^+}) = 0.2\ \mathrm{mol\ kg^{-1}}$

and $\mathrm{m}\,(\mathrm{SO_4{}^{2-}}) = 0.1\ \mathrm{mol\ kg^{-1}}$

Hence $\mathrm{I} = (1/2)\ [(0.2) + (2^2\mathrm{X}0.1)] = 0.3\ \mathrm{mol\ kg^{-1}}$

[2] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, , Reinhold, New York, 2nd. revised edn.1950, p.33.

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1.16.4: Ion-Water Interactions

The seminal paper in this subject was published in 1933 by Bernal and Fowler [1]. These authors drew attention to the possible impact of ions on water - water interactions in aqueous solutions beyond nearest-neighbour water molecules. The paper is also notable for the fact that the authors in their examination of the properties of ice, water and salt solutions did not use the term 'hydrogen bond' [2]. At that time there was much debate concerning the nature of this interaction bearing in mind that the 'valency' of hydrogen is unity. Rather Bernal and Fowler concluded that 'the unique properties of water are due to a structure of an extended complex characterized by tetrahedral co-ordination'.

Verwey drew attention to the importance of the interactions between an ion and near-neighbor water molecules in aqueous solution [3,4], these water molecules often being described as 'electrostricted ' by strong ion- solvent dipole interactions. Solvent water plays an important role in the control of partial molar entropies of ions in aqueous solutions [5] and transfer entropies of ions from aqueous to non-aqueous solvents [6].

A major landmark was a paper published by Frank and Evans who developed the concept that solutes, polar and apolar, have an important impact on water - water interactions in aqueous solutions [7]. In the development of models for ionic hydration, a distinction is drawn between hydrophilic and hydrophobic ions. Hydrophilic ions (alkali metal cations and halide anions) have strong attractive interactions with neighbouring dipolar water molecules. Neutron scattering data reveal important information concerning the arrangement of water molecules contiguous to ions [8-10].

For example in the case of chloride ions, the $\mathrm{Cl\text{–}\ H-0}$ configuration is essentially linear. Nevertheless, there is clear evidence, albeit often secondary, that strong water - ion interactions have an impact on water - water interactions beyond the immediate hydration sheath. Viscosity data indicate that ions, such as iodide and potassium, have a structure breaking effect. The cospheres, for these ions, are drawn, showing two parts [11,12]; an inner zone A and an outer zone B [11].

In zone A, ion - water dipole interactions are strong, leading to the general description ionichydration [12]. An indication of the structure of hydrated ions in solution emerges from X-ray crystallographic studies [13]. In the case of $\mathrm{KF.4H_2O}$, the structure comprises $\mathrm{K^+\ (H_2O)_6}$ and $\mathrm{F^-\ (H_2O)_6}$ octahedra; the $\mathrm{K^+ - O}$ distance is $0.279\ \mathrm{nm}$. Kebarle showed that mass spectrometry could be used to study ion - water interactions and, interestingly, step-wise hydration in the gas phase [14].

If a given ion in aqueous solution is indeed surrounded by two zones identified as zones A band B, the expectation is that ion - ion interactions in solution will reflect the impact of these structural features [15].

In the context of the impact of zone B, the suggestion was that with increase in size of ions so zone B should increase. Hence the expectation was that, for example, the partial molar isobaric heat capacity of tetra-n-butylammonium bromide in aqueous solution would be large in magnitude and negative in sign. Such not the case; the sign is positive [16,17]. A link was therefore established between the hydration characteristic of tetra-alkylammoniun ions and the structures of the corresponding salt hydrates [18]; e.g. tetra-iso-amylammonium fluoride hydrate, $\mathrm{(iso-Am)_4N^+\ F^-38\ H_2O}$ [19]. Generally, therefore, tetra-alkylammonium ions of $\mathrm{C_4 - C_9}$ carboxylates and tri-alkylsulphonium ions are often identified as hydrophobic where the interaction between these ions and neighboring water molecules is weak. [20-32]. Interestingly, constricting the alkyl chains to form azoniaspiroalkane cations diminishes the hydrophobic character [33,34]. The impact of replacing a hydrophobic terminal group in $\mathrm{R_4N^+}$ ions by a hydrophilic group on the properties of aqueous solutions is dramatic and offers an interesting insight into the role of ion – water interactions [35]. In contrast Finney and co-workers report that neutron diffraction data for aqueous solutions, containing $\mathrm{Me_4N^+\ Cl^-}$, show no evidence for increased ice-like structure compared to pure water [36]. Nevertheless thermodynamic and transport properties generally point to the conclusion that the ion $\mathrm{Me_4\ N^+}$ does not promote near-neighbor water-water hydrogen bonding [37,38].

Footnotes

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SECTION OVERVIEW

1.17: Isentropic and Iso-Variables

Topic hierarchy

1.17.1: Isentropic

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1.17.1: Isentropic

The term ‘adiabatic’ means that for a closed system no heat passes between system and surroundings; $\mathrm{q} = 0$. The term ‘isentropic’ introduces the further constraint that the system remains at equilibrium with the surroundings; i.e. the affinity for spontaneous change is zero. From the Second Law,

$$\mathrm{T\,dS} = \mathrm{q} + \mathrm{A\,d\xi} \quad \text{where } \mathrm{A\,d\xi} \geq 0$$

The isentropic condition means that both A and q are zero. Hence dS is zero, indicating that the entropy of the system remains constant. In other words, ‘isentropic’ describes an adiabatic change along an equilibrium and therefore reversible pathway.

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1.17.2: Isentropic Thermal Pressure Coefficient

The volume of a given closed system is defined by the following set of independent variables where ξ is the general composition variable.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \xi^{\mathrm{eq}}; \mathrm{A} = 0\right]$$

We have rather over-defined the system. The aim is to identify the composition variable at equilibrium and the condition that the affinity for spontaneous change is zero. The dependent variable entropy for this system is defined in analogous fashion; equation (b).

$$\mathrm{S} = \mathrm{S}\left[\mathrm{T}, \mathrm{p}, \xi^{\mathrm{eq}}; \mathrm{A} = 0\right]$$

The system is perturbed by a change in temperature along a path for which the affinity for spontaneous change is zero. Moreover the entropy of the system remains the same as that given in equation (b). In order to hold the latter condition the equilibrium pressure must change. In the state defined by the independent variables $[\mathrm{T}, \mathrm{p}, \xi^{eq}; \mathrm{A} = 0]$ the (equilibrium) isentropic differential dependence of pressure p on temperature is the isentropic thermal pressure coefficient, β_{S}; equation.(c).

$$\beta_{\mathrm{s}} = (\partial \mathrm{p}/\partial \mathrm{T})_{\mathrm{s}}$$

Further [1]

$$\beta_{\mathrm{S}} = (\partial \mathrm{S}/\partial \mathrm{V})_{\mathrm{T}}$$

Also [2],

$$\beta_{\mathrm{s}} = \sigma/\left(\mathrm{T}\,\alpha_{\mathrm{p}}\right)$$

Here σ is the isobaric heat capacity for unit volume (heat capacitance) of the system, $\mathrm{C_p}/\ \mathrm{V}$. The three isentropic properties α_{S}, κ_{S} and β_{S} are related using equation (f); [3].

$$\beta_{\mathrm{s}} = -\alpha_{\mathrm{s}}/\kappa_{\mathrm{s}}$$

With reference to the (equilibrium) thermal expansivity, α_{S}, we envisage that the temperature is changed to produce a change in volume along a path for which the entropy remains the same as in equation (b) and the affinity for spontaneous change remains at zero.

$$\alpha_{\mathrm{s}}(\mathrm{A} = 0) = \frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{s;A=0}}$$

In analogous fashion, κ_{S} is a measure of the change in volume produced by a change in pressure.

$$\kappa_{\mathrm{S}}(\mathrm{A} = 0) = -\frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{S;A=0}}$$

Footnotes

[1] From

$$\left[\frac{\partial}{\partial \mathrm{p}}\left(\frac{\partial \mathrm{H}}{\partial \mathrm{S}}\right)_{\mathrm{p}}\right]_{\mathrm{s}} = \left[\frac{\partial}{\partial \mathrm{S}}\left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{s}}\right]_{\mathrm{p}}$$

But at equilibrium where $\mathrm{A} = 0$, $T = \left(\frac{\partial H}{\partial S}\right)_P$ and $\mathrm{V} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{s}}$

Then

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{s}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{p}}$$

.

From $\beta_{\mathrm{s}} = \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{s}}$, Using the above Maxwell Relation,

$$\beta_S = \left(\frac{\partial S}{\partial V}\right)_T$$

[2] From the definition,

$$\beta_s = \left(\frac{\partial p}{\partial T}\right)_s$$

Using a calculus operation

$$\beta_s = -\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial S}\right)_T$$

From the Gibbs - Helmholtz Equation,

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

From a Maxwell equation, $\left(\frac{\partial S}{\partial T}\right)_p = -\left(\frac{\partial V}{\partial T}\right)_p$. Then

$$\beta_s = \frac{C_p}{T}\frac{1}{E_p}$$

But

$$E_p = V\,\alpha_p$$

Then,

$$\beta_s = \frac{C_p}{V}\frac{1}{T\,\alpha_p}$$

Or,

$$\beta_s = \sigma / T\,\alpha_p$$

[3] From the definition, $\beta_s = \left(\frac{\partial p}{\partial T}\right)_s$, then, $\beta_s = \left(\frac{\partial p}{\partial V}\right)_s \left(\frac{\partial V}{\partial T}\right)_s$ Then,

$$\beta_S = -E_S/K_s = -\left(E_S/V\right) / \left(K_s/V\right) = -\alpha_S/\kappa_S$$

Also from [2] and [3],

$$E_s/K_s = -\frac{C_p}{V}\frac{1}{T\,\alpha_p}$$

Then

$$\alpha_s/\kappa_s = -\sigma / T\,\alpha_p$$

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1.17.3: Iso-Variables

Isobaric: A given system is held at constant pressure.

Isothermal: A given system is held at constant temperature.

Isochoric: A given closed system is held at constant volume.

Isentropic: This condition, linked to the adiabatic constraint, requires that during a reversible change the entropy of a system remains constant in a particular thermodynamic process; e.g. compression. **Adiabatic + Reversible = Isentropic**. We can find isentropic processes which are irreversible. In this case they are not adiabatic.

Isolated System: The boundary insulates a given system from the surroundings . This is not really an iso-variable in the thermodynamic sense.

Isoperibol: In the vast majority of calorimetric experiments, the surroundings and the reaction vessel (the system+ container) are at constant temperature. When the experiment is initiated the composition of the closed system changes resulting from, for example, chemical reaction, mixing of liquids….. The temperature of the closed system changes albeit by a small amount because the processes taking place in the calorimeter are either exo- or endo-thermic. A sensitive detector is used to measure the change in temperature of the system. In pedantic terms the system is not constrained to be ‘isothermal’. So the calorimeter being used in such an experiment is an **isoperibol calorimeter**.

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1.17.4: Isochoric Properties

A given closed system is characterised by a given intensive variable X. In this section we have in mind an intensive property such as the relative permittivity of a liquid. The variable X may also refer to an equilibrium constant and related parameters such as the enthalpy of reaction, $\Delta_{\mathrm{r}}\mathrm{H}(\mathrm{T},\mathrm{p})$. In all cases we assert that the closed system is at thermodynamic equilibrium where the affinity for spontaneous change is zero. Thus we may define X for a given system in terms of the temperature and pressure.

$$\mathrm{X} = \mathrm{X}[\mathrm{T},\mathrm{p}]$$

The molar volume of the system is defined in analogous fashion.

$$\mathrm{V_m} = \mathrm{V_m}[\mathrm{T},\mathrm{p}]$$

Then

$$\mathrm{dV_m} = \left(\frac{\partial \mathrm{V_m}}{\partial \mathrm{T}}\right)_{\mathrm{p}} \mathrm{dT} + \left(\frac{\partial \mathrm{V_m}}{\partial \mathrm{p}}\right)_{\mathrm{T}} \mathrm{dp}$$

In other words the dependence of molar volume on T and p is characterised by the partial derivatives $\left(\frac{\partial \mathrm{V_m}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$ and $\left(\frac{\partial V_m}{\partial p}\right)_T$.

With equation (b) and (c) in mind we return the intensive property X described in equation (a). The dependence of X on T and p is similarly characterized by the two partial derivatives, $\left(\frac{\partial X}{\partial T}\right)_p$ and $\left(\frac{\partial \mathrm{X}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$. A calculus operation yields an equation for the partial derivative $\left(\frac{\partial \mathrm{X}}{\partial T}\right)_{\mathrm{V(m)}}$. Thus

$$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{T}}\right)_{\mathrm{V(m)}} = \left(\frac{\partial \mathrm{X}}{\partial \mathrm{T}}\right)_{\mathrm{p}} + \left(\frac{\partial \mathrm{X}}{\partial \mathrm{p}}\right)_{\mathrm{T}} \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V(m)}}$$

The property $\left(\frac{\partial \mathrm{X}}{\partial T}\right)_{\mathrm{V(m)}}$ is the isochoric differential dependence of X on T. Now (cf. equation (c)) volume \(\mathrm{V}_{\mathrm{m}}\) depends on T. Hence to hold $\mathrm{V_m}$ constant, the pressure has to change. In fact equation (c) is used to find the required change in pressure for a given change in T; equation (e).

$$\mathrm{dp} = -\left(\frac{\partial \mathrm{V_m}}{\partial \mathrm{T}}\right)_{\mathrm{p}} \left(\frac{\partial \mathrm{p}}{\partial \mathrm{V_m}}\right)_{\mathrm{T}} \mathrm{dT}$$

In other words the required change in pressure is determined by the equation of state for the system and is characteristic of the system, T and p. For a given change in temperature, $\delta\mathrm{T(exp)}$ there is a defined change in pressure, $\delta\mathrm{p(def)}$. The isochoric condition takes the following form granted that in the experiment we decide to change the temperature by an amount δT.

$$\mathrm{V_m}[\mathrm{T},\mathrm{p}] = \mathrm{V_m}[\mathrm{T} + \delta\mathrm{T(exp)};\mathrm{p} + \delta\mathrm{p(def)}]$$

We now return to the property X defined in equation (a). We consider the property X at the two conditions highlighted in equation (f);

$$\mathrm{X}[\mathrm{T},\mathrm{p}]; \quad \mathrm{X}[\mathrm{T} + \delta\mathrm{T(exp)};\mathrm{p} + \delta\mathrm{p(def)}]$$

The term $\left(\frac{\partial \mathrm{X}}{\partial \mathrm{T}}\right)_{\mathrm{V(m)[T,p]}}$ defines an isochoric dependence of X on T at pressure p and temperature T. At each temperature the isochoric dependence of X on T reflects the dependence of $\mathrm{V_m}$ on T.

The analysis outlined above is repeated but in terms of the isochoric dependence of X on pressure. In order that the volume of a system does not change when the pressure is changed by $\delta\mathrm{p(exp)}$, the temperature must be changed by an amount $\delta\mathrm{T(def)}$ determined by the equation of state for the system.

$$\mathrm{V_m}[\mathrm{T},\mathrm{p}] = \mathrm{V_m}[\mathrm{T} + \delta\mathrm{T(def)};\mathrm{p} + \delta\mathrm{p(exp)}]$$

We compare property X under the isochoric condition given in equation (h);

$$\mathrm{X}[\mathrm{T},\mathrm{p}]; \quad \mathrm{X}[\mathrm{T} + \delta\mathrm{T(def)};\mathrm{p} + \delta\mathrm{p(exp)}]$$

$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{p}}\right)_{\mathrm{V(m)[T,p]}}$ describes the isochoric dependence of X on pressure.

We have carefully examined the concept of an isochoric dependence of a given variable on either T or \(\mathrm{p}\). The reason for this care emerges from the observation that the literature describes a number of isochoric parameters. In some cases the analysis

is recognized as extrathermodynamic. In other cases a patina of thermodynamics is introduced into an analysis leading to further debate.

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1.17.5: Isochoric Thermal Pressure Coefficient

The equilibrium volume of a given closed system is defined by the following set of independent variables where ξ is the general composition variable.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \xi^{\mathrm{eq}}; \mathrm{A} = 0\right]$$

We have rather over-defined the system. The aim is to identify the composition variable at equilibrium and under the condition that the affinity for spontaneous change is zero. The system is perturbed by a change in temperature but we require that the system travels a path where the volume remains constant (and at equilibrium). The pressure must be changed in order to satisfy these conditions. By definition the isochoric differential dependence of pressure on temperature defines the isochoric thermal pressure coefficient.

$$\beta_V = \left(\frac{\partial p}{\partial T}\right)_v$$

Three interesting equations follow [1-3].

$$\beta_{\mathrm{V}} = \alpha_{\mathrm{p}}/\kappa_{\mathrm{T}}$$

$$\beta_{\mathrm{V}} = -\mathrm{C_V}/\mathrm{T}\,\mathrm{V}\,\alpha_{\mathrm{s}}$$

$$\alpha_{\mathrm{p}}/\kappa_{\mathrm{T}} = -\mathrm{C_V}/\mathrm{T}\,\mathrm{V}\,\alpha_{\mathrm{s}}$$

Footnotes

[1] From equation (a)

$$\beta_{\mathrm{V}} = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$$

Or,

$$\beta_{\mathrm{v}} = \mathrm{E_p}/\mathrm{K_T} = \alpha_{\mathrm{p}}/\kappa_{\mathrm{T}}$$

[2] Using a Maxwell relationship

$$\beta_V = \left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_S$$

But $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \mathrm{C_V}/\mathrm{T}$ Then

$$\beta_{\mathrm{v}} = -\mathrm{C_v}/\mathrm{T}\,\mathrm{E_s} = -\mathrm{C_v}/\mathrm{T}\,\mathrm{V}\,\alpha_{\mathrm{s}}$$

[3] From [1] and [2],

$$\mathrm{E_p}/\mathrm{K_T} = -\mathrm{C_V}/\mathrm{T}\,\mathrm{E_S}$$

Or,

$$\alpha_{\mathrm{p}}/\kappa_{\mathrm{T}} = -\mathrm{C_V}/\mathrm{T}\,\mathrm{V}\,\alpha_{\mathrm{S}}$$

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1.17.6: Isotonic Method; Isopiestic Method

The isotonic method is ‘beautifully simple’[1]. The technique, described as both Isotonic and Isopiestic, leads to osmotic coefficients for solvents and activity coefficients for solutes in solution, generally aqueous solutions. Authors reporting their results describe apparatus and procedures which often differ marginally from those of other authors. Scatchard and coworkers describe how six small platinum cups, volume approx. $15\ \mathrm{cm}^3$, are held in a gold-plated copper block, the cups being fitted with hinged lids [1]. The cups and copper block, filled with solutions (see below) are held in a partially evacuated thermostatted chamber. The copper block is rocked gently. Over a period of time the cups are removed, weighed and replaced.The experiment ends when the masses of solutions in the cups are constant.

The development of the isopiestic method can be traced to the experiments reported in 1917 by Bousfield[2] (who used the word, iso-piestic). A closed system was set up containing several solid salts in separate sample cells together with a little water(ℓ) in a separate sample cell. A little more water(ℓ) was added to the separate sample cell and the sample cells containing salts reweighed over a period of many days. The uptake of water by the salts was monitored, eventually forming salt solutions. A quantity h, the number of moles of water taken up by a mole of salt was calculated; e.g. $\mathrm{h} = 12.43(\mathrm{KCl}), 14.23(\mathrm{NaCl})\ \text{and}\ 17.18(\mathrm{LiCl})$. The system is isopiestic, meaning that all samples have equal vapour pressure. [One cannot help but feel sorry for Bousfield after reading the Discussion after the paper was presented at a meeting. The critics clearly did not appreciate what Bousfield was attempting to do.] Modern techniques developed from this approach[3].

To illustrate the technique, consider the case where just two cups, A and B, are used containing aqueous solutions of two salts, i and j. Spontaneous transfer of solvent water occurs through the vapour phase until eventually (often after many hours) equilibrium is attained and no change in mass occurs [4,5]. At equilibrium the chemical potentials of water in the two dishes are equal. Thus,

$$\mu_{\mathrm{j}}^{\mathrm{eq}}(\text{dish A}, \mathrm{T}, \mathrm{p}) = \mu_{\mathrm{i}}^{\mathrm{eq}}(\text{dish B}, \mathrm{T}, \mathrm{p})$$

Granted that the masses of salts used to prepare the solutions in the two cups are accurately known, the mass of cups at equilibrium yields the equilibrium molalities. In most studies one dish (e.g. dish A) holds a standard [e.g. $\mathrm{KCl(aq)}$] for which the dependence of practical osmotic coefficient on composition is accurately known.

If, for example, the two cups contain aqueous salt solutions, equation (a) is rewritten as follows granted that the pressure is close to ambient.

$$[\mu_1^*(\ell) - \phi_{\mathrm{j}}\,\mathrm{R}\,\mathrm{T}\,\mathrm{v_j}\,\mathrm{m_j}]_{\mathrm{A}} = [\mu_1^*(\ell) - \phi_{\mathrm{i}}\,\mathrm{R}\,\mathrm{T}\,\mathrm{v_i}\,\mathrm{m_i}]_{\mathrm{B}}$$

Here $\mathrm{m_i}$ and $\mathrm{m_j}$ are the equilibrium molalities, where the word ‘equilibrium’ refers to the solvent water. Hence

$$(\phi_{\mathrm{j}}\,\mathrm{v_j}\,\mathrm{m_j})_{\mathrm{A}} = (\phi_{\mathrm{i}}\,\mathrm{v_i}\,\mathrm{m_i})_{\mathrm{B}}$$

The isopiestic ratio $\mathrm{R_{iso}}$ is defined by equation (d).

$$\mathrm{R_{iso}} = (\mathrm{v_i}\,\mathrm{m_i})_{\mathrm{B}} \,/\, (\mathrm{v_j}\,\mathrm{m_j})_{\mathrm{A}}$$

Hence,

$$\phi_{\mathrm{B}} = \phi_{\mathrm{A}}/\mathrm{R_{iso}}$$

Therefore ϕ_{B} is obtained from the experimentally determined $\mathrm{R_{iso}}$ and a known (i.e. previously published standard) ϕ_{B}.

In general terms, an ‘isopiestic experiment’ is based around the properties of the solvent water in a given solution. But the aim of the experiment is to gain information about the activity coefficient of the solute. The calculation therefore relies on the Gibbs - Duhem Equation . According to the Gibbs – Duhem equation the dependence of chemical potentials of salt and solvent are linked . If a given solution comprises $\mathrm{n_1}$ moles of water and $\mathrm{n_j}$ moles of solute, then

$$\mathrm{n_1}\ (\mathrm{d}\mu_1/\mathrm{dnn_j}) + \mathrm{n_j}\ (\mathrm{d}\mu_{\mathrm{j}}/\mathrm{dn_j}) = 0$$

For a solution molality $\mathrm{m_j}$ in a solvent, molar mass $\mathrm{M_1}$

$$(1/\mathrm{M_1})\ \mathrm{d}\mu_1/\mathrm{dmm_j} + \mathrm{m_j}\,\mathrm{d}\mu_{\mathrm{j}}/\mathrm{dm_j} = 0$$

Then if pressure p is close to the standard pressure,

$$(1/M_1)\ d\left[\mu_1^*(\ell) - \phi\, R\, T\, M_1\, m_j\right]/dm_j + m_j\, d\left[\mu_j^0(aq) + R\, T\, \ln\left(m_j\, \gamma_j/m^0\right)\right]/dm_j = 0$$

Or,

$$-\phi - m_j\, d\phi/dm_j + 1 + m_j\, d\ln\left(\gamma_j\right)/dm_j = 0$$

Thus

$$-\left(\phi/m_j\right) - d\phi/dmm_j + \left(1/m_j\right) + d\ln\left(\gamma_j\right)/dmm_j = 0$$

No further progress can be made until we have determined in a series of experiments the dependence of ϕ on m_j. The dependence of ϕ_B on molality m_B is obtained after many experiments. In a common procedure the dependence is fitted to a polynomial in mj such that integration yields the activity coefficient for the solute γ_j. Suppose for example we find that for a given system ϕ is a linear function of molality m_j. Thus

$$\phi = 1 + a\, m_j$$

Or,

$$d\phi/dm_j = a$$

Hence,

$$\ln\left(\gamma_j\right) = 2\, a\, m_j$$

We note how the analysis relies on the fact the solute and solvent ‘communicate with each other’.

Footnotes

[1] G. Scatchard, W.J.Hamer and S.E.Wood, J.Am.Chem.Soc.,1938,**60**,3061.

[2] W. R. Bousfield, Trans. Farady Soc.,1917,**13**,401.

[3] J. A.Rard and R. F. Platford, Activity Coefficients in Electrolyte Solutions, ed. K. S. Pitzer, CRC Press, Boca Raton, 2nd edition, 1991.

[4] In fact one can regard the phenomenon as osmosis, the vapour phase being a perfect semi-permeable membrane.

[5] The system is partially evacuated so that equilibrium vapour pressure is reasonably rapidly attained.

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1.17.7: Isopiestic: Aqueous Salt Solutions

An extensive literature reports applications of the isopiestic technique to the determination of osmotic coefficients and ionic activity coefficients for salt solutions [1-11]. In effect the technique probes the role of ion-ion interactions in determining the properties of real salt solutions.

Several approaches have been reported for analyzing isopiestic results. A common method starts with the isopiestic ratio $\mathrm{R_{iso}}$. For solutions in dishes A and B at equilibrium, the isopiestic equilibrium conditions is given by equation (a).

$$(\phi_j V_j m_j)_A = (\phi_i V_i m_i)_B$$

The isopiestic ratio,

$$\mathrm{R_{iso}} = (\mathrm{v_i\, m_i})_\mathrm{B} / (\mathrm{v_j\, m_j})_\mathrm{A}$$

An important task formulates an equation relating the osmotic coefficient for a given salt solution and the mean ionic coefficient $\gamma_\pm$

If the salt solution contains a single salt, then according to the Gibbs-Duhem Equation,

$$(1/M_1)\ d\mu_1(aq) = -m_j\, d\mu_j(aq)$$

Hence (where pressure p is close to the standard pressure)

$$\begin{aligned}(1/\mathrm{M_1})\ \mathrm{d}\left[\mu_1^*(\mathrm{l}) - (\phi\, \mathrm{R\, T\, v\, M_1\, m_j})\right] = \\ -\mathrm{m_j\, d}\left[\mu_\mathrm{j}^0(\mathrm{aq}) + \left(\mathrm{v\, Q\, R\, T\ ln}\left(\mathrm{m_j}\,\gamma_\pm/\mathrm{m^0}\right)\right]\end{aligned}$$

Then,

$$\mathrm{d}\left[\phi\, \mathrm{m_j})\right] = -\mathrm{m_j\, d}\left[(\ln(\mathrm{m_j}) + \ln(\gamma_\pm)\right]$$

Or,

$$-\phi\, \mathrm{dm_j} - \mathrm{m_j\, d}[\phi)] = -\mathrm{m_j}\ [\mathrm{d}(\mathrm{m_j})/\mathrm{m_j} + \mathrm{d}\ln(\gamma_\pm)]$$

Equation (f) is integrated between the limits '$\mathrm{m_j} = 0$' and $\mathrm{m_j}$ [3,4]. Then,

$$\ln(\gamma_\pm) = (\phi - 1) + \int_0^{m(j)} (\phi - 1)\, d\ln(m_j)$$

And,

$$\phi = 1 + \frac{1}{m_j} \int_0^{m(j)} m_j\, d\ln(\gamma_\pm)$$

Hence the dependences of both $\gamma_\pm$ and ϕ are obtained [1] for salt solutions and of both $\gamma_\mathrm{j} and \(\phi$ for solutions containing neutral solutes [5].

An important challenge at this stage is to express the experimentally determined dependence of ϕ on $\mathrm{m_j}$. Having expressed this dependence quantitively, the dependence of $\gamma_\pm$ on $\mathrm{m_j}$ is obtained using equation (g). The integration can be done graphically [6] or numerically using a computer- based analysis. The Debye-Huckle Limiting Law plus extended form can be used to express the dependence of ϕ on $\mathrm{m_j}$.

$$\phi = 1 - (\mathrm{S_\gamma}/3)\ \left(\mathrm{m_j}/\mathrm{m^0}\right) + \sum_{\mathrm{i=1}}^{\mathrm{i=j}} \mathrm{A_i}\ \left(\mathrm{m_j}/\mathrm{m^0}\right)^{\mathrm{r(i)}}$$

The parameter $\mathrm{r(i)}$ increases in quarter powers. Then [7,8],

$$\ln(\gamma_\pm) = -\mathrm{S_\gamma}\ \left(\mathrm{m_j}/\mathrm{m^0}\right)^{1/2} + \sum_{\mathrm{i=1}}^{\mathrm{i=j}} \mathrm{A_i}\ \left(\frac{\mathrm{r_i}+1}{\mathrm{r_i}}\right)\ \left(\mathrm{m_j}/\mathrm{m^0}\right)^{\mathrm{r(i)}}$$

In more recent accounts, Pitzer's equations have been used to represent the dependence of ϕ on ionic strength [9,10].

If the isopiestic experiments are repeated at several temperatures, the relative partial molar enthalpy of the solvent $L_1(aq)$ is obtained [10].

In summary a large scientific literature reports thermodynamic data for aqueous solutions containing salts [11] and mixed salt [12] systems.

Footnotes

[1] G. Scatchard, W. J. Hamer and S. E. Wood, J.Am.Chem.Soc.,1938,**60**,3061.

[2] For reviews and further data compilations see

a. R. N. Goldberg and R. L. Nuttall, J.Phys.Chem.Ref.Data, 1978,**7**,263.
b. E. C. W. Clarke, J.Phys.Chem.Ref.Data, 1985,**14**,489.

[3] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd edn. (revised), 1965, p. 34.

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d. C. C. Briggs, R. Charlton and T. H. Lilley, J. Chem.Thermodyn., 1973, **5**, 445; $HClO_4 + NaClO_4 + LiClO_4(aq)$.
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i. W.-Y. Wen, S.Saito and C-m. Lee, J. Phys. Chem.,1966,**70**,1244; $R_4NF(aq)$.
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SECTION OVERVIEW

1.18: Liquid Mixtures

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1.18.1: Liquid Mixtures: Regular Mixtures

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1.18.3: Liquid Mixtures: Series Functions for Activity Coefficients

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1.18.5: Liquid Mixtures: Binary: Pseudo-Excess Properties

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1.18.1: Liquid Mixtures: Regular Mixtures

A given binary liquid mixture is prepared using liquid-1 and liquid –2 at temperature T and pressure p, the latter being close to the standard pressure. The chemical potentials, $\mu_1\,(\mathrm{mix};x_1)$ and $\mu_2\,(\mathrm{mix};x_2)$ are related to the mole fraction composition, x_1 and $x_2(=1-x_1)$ using equations (a) and (b) where $\mu_1^*(\ell)$ and $\mu_2^*(\ell)$ are the chemical potentials of the two pure liquid components at the same T and p;

$$\mu_1\,(\mathrm{mix};\mathrm{x_1}) = \mu_1^*(\ell) + \mathrm{R\,T\,\ln\left(x_1\,f_1\right)}$$

$$\mu_2\,(\mathrm{mix};x_2) = \mu_2^*(\ell) + RT\,\ln\left(x_2\,f_2\right)$$

Here for both $\mathrm{i}=1,2$ at all T and p,

$$\mathrm{limit}\,(x_i \to 1)\,f_i = 1$$

The term “regular mixture” describes a liquid mixture for which the rational activity coefficients $\mathrm{f_1}$ and $\mathrm{f_2}$ are given by equations (d) and (e) where the property w is independent of temperature and liquid mixture composition [1-5].

$$\ln\left(f_1\right) = \left(w/RT\right)x_2^2$$

$$\ln\left(f_2\right) = \left(w/RT\right)\,\left(1-x_2\right)^2$$

Then, for example, at all T and p [6],

$$\mathrm{limit}\,(x_2 \to 0)\ln\left(f_1\right) = 0; f_1 = 1$$

Similarly,

$$\mathrm{limit}\,(x_2 \to 1)\ln\left(f_2\right) = 0; f_2 = 1$$

Interest in regular liquid mixtures stems from the observation that the properties of such real (as opposed to ideal) mixtures are simply described. Of course the term “real” only means that the dependences of rational activity coefficients on mole fraction composition are defined by equations (d) and (e) and that the thermodynamic properties of the liquid mixture are not ideal.

For example, according to equation (d),

$$d\ln\left(f_1\right)/dT = -\left(w/RT^2\right)\,x_2^2$$

With reference to the dependence of the properties of binary liquid mixtures on temperature (at fixed pressure), equation (a) yields equation (i).

$$\frac{\mathrm{d}\left[\mu_1(\mathrm{mix})/\mathrm{T}\right]}{\mathrm{dT}} = \frac{\mathrm{d}\left[\mu_1^*(\ell)/\mathrm{T}\right]}{\mathrm{dT}} + \mathrm{R}\left[\frac{\mathrm{d\ln\left(f_1\right)}}{\mathrm{dT}}\right]$$

From the Gibbs - Helmholtz equation,

$$-\frac{\mathrm{H_1(mix)}}{\mathrm{T^2}} = -\frac{\mathrm{H_1^*(\ell)}}{\mathrm{T^2}} - \mathrm{R}\left(\frac{\mathrm{w}}{\mathrm{R\,T^2}}\right)\mathrm{x_2^2}$$

Hence

$$\mathrm{H_1(mix) = H_1^*(\ell) + w\,x_2^2}$$

Here

$$\mathrm{limit}\,(\mathrm{x_2} \to 0)\,\mathrm{H_1(mix)} = \mathrm{H_1^*(\ell)}$$

According to equation (k), $\mathrm{H_1(mix)}$ is a quadratic function of the mole fraction composition.

Further [7],

$$\mathrm{S_1(mix) = S_1^*(\ell) - R\,\ln\left(x_1\right)}$$

Hence entropic properties of regular mixtures do not deviate from the properties of an ideal liquid mixture. In terms of excess properties for regular mixtures, $S_m^E = 0$ and therefore $\mathrm{G_m^E = H_m^E}$. Equations (d) and (e) can be written as explicit equations for $\mathrm{f_1}$ and

f_2 respectively.

$$f_1 = \exp\left[\left(\frac{w}{RT}\right)\, x_2^2\right]$$

$$f_2 = \exp\left[\left(\frac{w}{RT}\right)\, (1-x_2)^2\right]$$

The partial pressures of the two chemical substances are given by Raoult's Law.

$$\mathrm{p_1 = p_1^* x_1\ exp\left[\left(\frac{W}{R\,T}\right)\, x_2^2\right]}$$

$$\mathrm{p_2 = p_2^* x_2\ exp\left[\left(\frac{w}{R\,T}\right)\, (1-x_2)^2\right]}$$

For both liquid components, deviations from ideal thermodynamic properties increase with increase in the magnitude of $(\mathrm{w/R\,T})$. If $\mathrm{w} > 0$, the deviations are called positive whereas if $\mathrm{w} < 0$ the deviations are called negative. In the event that $(\mathrm{w/R\,T})$ equals 2, the plots of $\mathrm{p_1}$ and $\mathrm{p_2}$ against mole fraction composition are horizontal when $x_1 = x_2 = 0.5$. But in the event that $(\mathrm{w/R\,T})$ equals 3, a range of binary liquid mixtures exist having intermediate mole fraction compositions and are unstable. These mixtures separate into two liquid mixtures, one rich in component 1 and the other rich in component 2.

Footnotes

[1] J. Hildebrand, J Am. Chem. Soc.,1929, **51**,69. Accounts of this class of mixtures are given in references [2]-[5].

[2] E. A. Guggenheim, Thermodynamics, North Holland Publishing Company, Amsterdam, 1950, chapter 5; note that Guggenheim uses the symbol x to represent the mole fraction composition of a binary liquid mixture x_2; see page 173.

[3] E. A. Guggenheim, Mixtures, Clarendon Press, Oxford, 1952, chapter IV.

[4] M.L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979, chapter 16.

[5] G. N. Lewis and M. L. Randall, Thermodynamics, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961, chapter 21.

[6]

$$\mathrm{R\,T = \left[JK^{-1}\ mol^{-1}\right]\ [K] = \left[Jmol^{-1}\right]}$$

Then, $\mathrm{w = \left[Jmol^{-1}\right]}$, a molar energy.

[7] From, $\mu_1(\mathrm{mix}) = \mathrm{H_1(mix) - T\,S_1(mix)}$

$$\mathrm{\mu_1^*(\ell) + R\,T\ ln\,(x_1) + w\,x_2^2 = H_1^*(\ell) + w\,x_2^2 - T\,S_1(mix)}$$

Or,

$$\mathrm{\mu_1^*(\ell) - H_1^*(\ell) + R\,T\ ln\,(x_1) = -T\,S_1(mix)}$$

Or,

$$\mathrm{-T\,S_1''(\ell) + R\,T\ ln\,(x_1) = -T\,S_1(mix)}$$

[8] From equation (p) with $(w/R\,T) = 2$,

$$
\begin{aligned}
&\mathrm{p_1 = p_1^* x_1 \exp\left(2 x_2^2\right)} \\
&p_1 = p_1^* x_1 \exp\left[2\left(1-x_1\right)^2\right] \\
&\frac{\mathrm{d\left(p_1/p_1^*\right)}}{\mathrm{dx_1}} = \exp\left[2\left(1-\mathrm{x_1}\right)^2\right] - \mathrm{x_1}\, 4\left(1-\mathrm{x_1}\right) \exp\left[2\left(1-\mathrm{x_1}\right)^2\right] \\
&= \exp\left[2\left(1-x_1\right)^2\right]\left[1-4x_1\left(1-x_1\right)\right] \\
&= \exp\left[2\left(1-x_1\right)^2\right]\left[1-4x_1+4x_1^2\right] \\
&\frac{\mathrm{d\left(p_1/p_1^*\right)}}{\mathrm{dx_1}} = \exp\left[2\left(1-\mathrm{x_1}\right)^2\right]\left(1-2\,\mathrm{x_1}\right)^2 \\
&\frac{\mathrm{d\left(p_2/p_2^*\right)}}{\mathrm{dx_2}} = \exp\left[2\left(1-\mathrm{x_2}\right)^2\right] + \mathrm{x_2}\left(-4\right)\left(1-\mathrm{x_2}\right) \exp\left[2\left(1-\mathrm{x_2}\right)^2\right] \\
&\frac{\mathrm{d\left(p_2/p_2^*\right)}}{\mathrm{dx_2}} = \exp\left[2\left(1-\mathrm{x_2}\right)^2\right]\left(1-2\,\mathrm{x_2}\right)^2
\end{aligned}
$$

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1.18.2: Liquid Mixtures: General Equations

A given binary liquid mixture is prepared using liquid-1 and liquid –2 at temperature T and pressure p, the latter being close to the standard pressure. The chemical potentials, $\mu_1\,(\mathrm{mix};\mathrm{x}_1)$ and $\mu_2\,(\mathrm{mix};\mathrm{x}_2)$ are related to the mole fraction composition, x_1 and $x_2(=1-x_1)$ using equations (a) and (c) where $\mu_1^*(\ell)$ and $\mu_2^*(\ell)$ are the chemical potentials of the two pure liquid components at the same T and p;

$$\mu_1\,(\mathrm{mix};\mathrm{x}_1) = \mu_1^*(\ell) + \mathrm{R\,T}\,\ln\left(\mathrm{x}_1\,\mathrm{f}_1\right)$$

where

$$\mathrm{limit}\,(x_1 \to 1)\,f_1 = 1$$

$$\mu_2\,(\mathrm{mix};\mathrm{x}_2) = \mu_2^*(\ell) + \mathrm{R\,T}\,\ln\left(\mathrm{x}_2\,\mathrm{f}_2\right)$$

where

$$\mathrm{limit}\,(\mathrm{x}_2 \to 1)\,\mathrm{f}_2 = 1$$

A general equation for activity coefficient f_1 takes the following form [1].

$$\ln\left(f_1\right) = \sum_{k=1}^{k=\infty} \alpha_k\, x_s^{\lambda(k)}$$

Equation (e) satisfies the condition,

$$\mathrm{limit}\,(x_2 \to 0)\,\ln\left(f_1\right) = 0; f_1 = 1$$

The parameter α_k is characteristic of the mixture, temperature and pressure. The property λ_k is a real number. In the limit that the liquid mixture is dilute in chemical substance liquid-2, equation (e) simplifies to equation (g).

$$\ln\left(f_1\right) = \alpha\, x_2^{\lambda}$$

In general terms [2],

$$x_1\, d\ln\left(f_1\right) + x_2\, d\ln\left(f_2\right) = 0$$

We combine equations (e) and (h) with $\lambda_k \geq 2$ [3].

$$\frac{\mathrm{d}\ln\left(\mathrm{f}_1/\mathrm{f}_2\right)}{\mathrm{dx}_2} = \frac{1}{\mathrm{x}_2}\,\frac{\mathrm{d}\ln\left(\mathrm{f}_1\right)}{\mathrm{dx}\mathrm{x}_2} = \sum_{\mathrm{k}=1}^{\mathrm{k}=\infty} \alpha_\mathrm{k}\,\lambda_\mathrm{k}\,\mathrm{x}_2^{\lambda(\mathrm{k})-2}$$

Equation (i) is integrated to yield equation (j) where I is the constant of integration.

$$\ln\left(f_2\right) = \ln\left(f_1\right) - \sum_{k=1}^{k=\infty} \frac{\alpha_k\,\lambda_k\,x_2^{\lambda(k)-1}}{\lambda_k - 1} - I$$

Hence [4,5]

$$\begin{aligned}\ln\left(f_2\right) &= \ln\left(f_1\right) - \sum_{k=1}^{k=\infty} \frac{\alpha_k\,\lambda_k}{\lambda_k - 1}\,\left(x_2^{\lambda(k)-1} - 1\right) - \sum_{k=1}^{k=\infty} \alpha_k \\ &= \ln\left(f_1\right) - \sum_{k=1}^{k=\infty} \alpha_k\,\left[\frac{\lambda_k}{\lambda_k - 1}\,\left(x_2^{\lambda-(k-1)} - 1\right) - 1\right]\end{aligned}$$

In other words, granted that $\ln\left(f_1\right)$ is known as a function of x_2, then $\ln\left(f_2\right)$ can be calculated.

Footnotes

[1] I. Prigogine and R. Defay, Chemical Thermodynamics, transl. D. H. Everett, Longmans Green, London, 1954.

[2] For a binary liquid mixture , the Gibbs-Duhem equation relates activity coefficients f_1 and f_2. Thus,

$$-S\,dT + V\,dp + n_1\,d\mu_1 + n_2\,d\mu_2 = 0$$

At fixed T and p, $\mathrm{n_1\,d\mu_1 + n_2\,d\mu_2 = 0}$

Divide by $(n_1 + n_2)$; $x_1\,d\mu_1 + x_2\,d\mu_2 = 0$

$$\mathrm{x_1\,d\,[\mu_1^*(\ell) + R\,T\,\ln(x_1\,f_1)] + x_2\,d\,[\mu_2^*(\ell) + R\,T\,\ln(x_2\,f_2)] = 0}$$
$$\mathrm{x_1\,d\ln(x_1\,f_1) + x_2\,d\ln(x_2\,f_2) = 0}$$
$$\mathrm{x_1\,d\ln(x_1) + x_1\,d\ln(f_1) + x_2\,d\ln(x_2) + x_2\,d\ln(f_2) = 0}$$

But

$$\mathrm{x_1\,d\ln(x_1) + x_2\,d\ln(x_2) = (x_1/x_1)\;dxx_1 + (x_2/x_2)\;dxx_2}$$

Also $\mathrm{x_1 + x_2 = 1}$ so that $\mathrm{dx_1 + dx_2 = 0}$

[3] From equation (h) for a binary liquid mixture at fixed T and p,

$$(1 - x_2)\;\frac{d\ln(f_1)}{dx_2} + x_2\,\frac{d\ln(f_2)}{dx_2} = 0$$
$$\frac{d\ln(f_1)}{dx_2} - x_2\,\frac{d\ln(f_1)}{dx_2} + x_2\,\frac{d\ln(f_2)}{dx_2} = 0$$

We divide by x_2 and rearrange the equation.

$$\mathrm{\frac{d\ln(f_1)}{dxx_2} - \frac{d\ln(f_2)}{dx_2} = \frac{1}{x_2}\,\frac{d\ln(f_1)}{dxx_2}}$$

Or,

$$\mathrm{\frac{d\ln(f_1/f_2)}{dxx_2} = \frac{1}{x_2}\,\frac{d\ln(f_1)}{dx_2}}$$

[4] From equations (e) and (j),

$$\ln(f_2) = \sum_{k=1}^{k=\infty} \alpha_k\,x_2^{\lambda(k)} - \sum_{k=1}^{k=\infty} \frac{\alpha_k\,\lambda_k\,x_2^{\lambda(k)-1}}{\lambda_k - 1} - I$$

But at $x_2 = 1, f_2 = 1$. Then,

$$\mathrm{0 = \sum_{k=1}^{k=\infty} \alpha_k - \sum_{k=1}^{k=\infty} \frac{\alpha_k\,\lambda_k}{\lambda_k - 1} - I}$$

[5] J. N. Bronsted and P. Colmart, Z. Phys. Chem.,1934,**A168**, 381 (as quoted in reference 1).

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1.18.3: Liquid Mixtures: Series Functions for Activity Coefficients

A given binary liquid mixture is prepared using liquid-1 and liquid-2 at temperature T and pressure p, the latter being close to the standard pressure. The chemical potentials, $\mu_1\,(\text{mix};x_1)$ and $\mu_2\,(\text{mix};\text{x}_2)$ are related to the mole fraction composition, x_1 and $\text{x}_2\,(=1-\text{x}_1)$ using equations (a) and (c) where $\mu_1^*(\ell)$ and $\mu_2^*(\ell)$ are the chemical potentials of the two pure liquid components at the same T and p;

$$\mu_1\,(\text{mix};\text{x}_1) = \mu_1^*(\ell) + RT\,\ln\,(\text{x}_1\,\text{f}_1)$$

where

$$\text{limit}\,(x_1 \to 1)\,f_1 = 1$$

$$\mu_2\,(\text{mix};\text{x}_2) = \mu_2^*(\ell) + \text{R}\,\text{T}\,\ln\,(\text{x}_2\,\text{f}_2)$$

where

$$\text{limit}\,(\text{x}_2 \to 1)\,\text{f}_2 = 1$$

A quite general approach to understanding the properties of binary liquid mixtures expresses, for example, $\ln\,(f_1)$ as a series function in terms of mole fraction x_2 at fixed T and p. Using only three terms we obtain equation (e).

$$\ln\,(f_1) = \alpha_2\,x_2^2 + \alpha_3\,x_2^3 + \alpha_4\,x_2^4$$

As required,

$$\text{limit}\,(x_2 \to 0)\,\ln\,(f_1) = 0;\, f_1 = 1$$

Hence [1],

$$\begin{aligned}\ln\,(f_2) = {} & [\alpha_2 + (3/2)\,\alpha_3 + 2\,\alpha_4]\;x_1^2 \\ & - [\alpha_3 + (8/3)\,\alpha_4]\;x_1^3 + \alpha_4\,x_1^4\end{aligned}$$

As required, $\text{limit}\,(x_1 \to 0)\,\ln\,(f_2) = 0;\, f_2 = 1$

Footnotes

[1] From, $\ln\,(f_1) = \alpha_2\,x_2^2 + \alpha_3\,x_2^3 + \alpha_4\,x_2^4$

$$\ln\,(f_1) = \alpha_2\,(1-x_1)^2 + \alpha_3\,(1-x_1)^3 + \alpha_4\,(1-x_1)^4$$

Then

$$\frac{\text{d}\ln\,(f_1)}{dx_1} = -2\,\alpha_2\,(1-x_1) - 3\,\alpha_3\,(1-x_1)^2 - 4\,\alpha_4\,(1-x_1)^3$$

But from the Gibbs-Duhem equation (at fixed T and p)

$$x_1\,\frac{d\ln\,(f_1)}{dx_1} + x_2\,\frac{d\ln\,(f_2)}{dx_1} = 0$$

Or,

$$\frac{\text{d}\ln\,(f_2)}{\text{dx}_1} = -\frac{\text{x}_1}{\text{x}_2}\,\frac{\text{d}\ln\,(\text{f}_1)}{\text{dx}_1}$$

Or,

$$\frac{d\ln\,(f_2)}{dx_1} = -\frac{x_1}{(1-x_1)}\,\frac{d\ln\,(f_1)}{dx_1}$$

Then,

$$\frac{\text{d}\ln\,(\text{f}_2)}{\text{dx}_1} = 2\,\alpha_2\,\text{x}_1 + 3\,\text{x}_1\,\alpha_3\,(1-\text{x}_1) + 4\,\alpha_4\,\text{x}_1\,(1-\text{x}_1)^2$$

$$\frac{d\ln(f_2)}{dx_1} = 2\,\alpha_2\,x_1 + 3\,x_1\,\alpha_3 - 3\,\alpha_3\,x_1^2 + 4\,\alpha_4\,x_1 - 8\,\alpha_4\,x_1^2 + 4\,\alpha_4\,x_1^3$$

Or,

$$\frac{d\ln(f_2)}{dx_1} = [2\,\alpha_2 + 3\,\alpha_3 + 4\,\alpha_4]\;x_1 - [3\,\alpha_3 + 8\,\alpha_4]\;x_1^2 + 4\,\alpha_4\,x_1^3$$

The latter equation is integrated.

$$\ln(f_2) = [\alpha_2 + (3/2)\,\alpha_3 + 2\,\alpha_4]\;x_1^2 - [\alpha_3 + (8/3)\,\alpha_4]\;x_1^3 + \alpha_4\,x_1^4$$

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1.18.4: Liquid Mixtures: Binary: Less Common Properties

For an ideal liquid mixture containing i-liquid components four important molar properties are related to the corresponding properties of the pure liquid components using the following equations.

$$C_{V m_m}(\text{mix; id}) = \sum_i x_i \left\{ 1 - \left[\frac{E^*_{pi}(\ell)}{C^*_{V_i}(\ell)} \right] \left[\beta_v(\text{mix; id}) - \beta^*_{V_i}(\ell) \right] C^*_{V_i}(\ell) \right\}$$

$$E_{Sm}(\text{mix; id}) = \sum_i x_i \left\{ 1 - \left[\frac{C^*_{pi}(\ell)}{E^*_{Si}(\ell)} \right] \left[[\beta_v(\text{mix; id})]^{-1} - [\beta^*_{v_i}(\ell)]^{-1} \right] E^*_{Si}(\ell) \right\}$$

$$E_{Sm}(\text{mix; id}) = \sum_i x_i \left\{ 1 - \left[\frac{K^*_{pi}(\ell)}{E^*_{Si}(\ell)} \right] \left[\beta_s(\text{mix; id}) - \beta^*_{Si}(\ell) \right] E^*_{Si}(\ell) \right\}$$

$$K_{Sm}(\text{ mix; id }) = \sum_i x_i \left\{ 1 - \left[\frac{E^*_{pl}(\ell)}{K^*_{Si}(\ell)} \right] \left[\left[\beta_s(\text{ mix; id }) \right]^{-1} - [\beta^*_{si}(\ell)]^{-1} \right] K^*_{Si}(\ell) \right\}$$

With reference to these four equations, interesting features emerge. If $V^*_1(\ell)$ and $V^*_2(\ell)$ for the two components of a binary liquid mixture having ideal thermodynamic properties are linearly related at different temperatures and pressures then at fixed liquid mixture composition,

$$\left(\frac{\partial p}{\partial T} \right)_{v^*_1(1)} = \left(\frac{\partial p}{\partial T} \right)_{v^*_2(1)} = \left(\frac{\partial p}{\partial T} \right)_{v_{(mix;d)}}$$

Or,

$$\beta^*_{v_1}(\ell) = \beta^*_{v_2}(\ell) = \beta_v(\text{mix; id})$$

Under these conditions the two properties described in equations (a) and (b) are given by the mole fraction weighted sums of the properties of the pure liquids. The internal pressure pint is given by $[T\,\beta_V - 1]$. Hence the same condition holds with respect to the two properties defined by equations (a) and (b) if the internal pressures are equal. In practice liquids have different internal pressures. However this difference is often small for chemically similar liquids.

An interesting feature emerges if the molar entropies of the two liquids are linearly related over a range of temperatures and pressures. Thus,

$$\left(\frac{\partial p}{\partial T} \right)_{s^*_1(\theta)} = \left(\frac{\partial p}{\partial T} \right)_{s^*_2(\theta)} = \left(\frac{\partial p}{\partial T} \right)_{S(\text{ mid; ;d})}$$

Or,

$$\beta^*_{s1}(\ell) = \beta^*_{S2}(\ell) = \beta_s(\text{mix; id})$$

Therefore a liquid mixture where the components have identical isentropic thermal pressure coefficients, $K_{Sm}(\text{mix; id})$ and $E_{Sm}(\text{mix; id})$ are given by the mole fraction weighted sums of the properties of the pure components [1].

In the case of an ideal binary liquid mixture the following three equations relate the isochoric heat capacities, isentropic compressions and isentropic expansions to the properties of the component pure liquids.

$$C_{Vm}(\text{mix; id}) = x_1\,C^*_{v1}(\ell) + x_2\,C^*_{V2}(\ell) + T\left\{ \left[\frac{x_1\,\left[E^*_{p1}(\ell)\right]^2}{K^*_{T1}(\ell)} \right] + \left[\frac{x_2\,\left[E^*_{p2}(\ell)\right]^2}{K^*_{T2}(\ell)} \right] - \left[\frac{\left[x_1\,E^*_{p1}(\ell) + x_2\,E^*_{p2}(\ell)\right]^2}{x_1\,K^*_{T1}(\ell) + x_2\,K^*_{T2}(\ell)} \right] \right\}$$

$$K_{Sm}(mix;id) = x_1\,K^*_{S1}(\ell) + x_2\,K^*_{S2}(\ell)$$
$$+\,T\left\{\left[\frac{x_1\,\left[E^*_{p1}(\ell)\right]^2}{C^*_{p1}(1\ell)}\right] + \left[\frac{x_2\,\left[E^*_{p2}(\ell)\right]^2}{C^*_{p2}(\ell)}\right] - \left[\frac{\left[x_1\,E^*_{pl}(\ell) + x_2\,E^*_{p2}(\ell)\right]^2}{x_1\,C^*_{p1}(\ell) + x_2\,C^*_{p2}(\ell)}\right]\right\}$$

$$E_{Sm}(mix;id) = x_1\,E^*_{Sl}(\ell) + x_2\,E^*_{S2}(\ell)$$
$$+\,T\left\{\begin{array}{l}\left[\frac{x_1\,K^*_{T1}(\ell)\,C^*_{p1}(\ell)}{E^*_{p1}(\ell)}\right] + \left[\frac{x_2\,K^*_{T2}(\ell)\,C^*_{p2}(\ell)}{E^*_{p2}(\ell)}\right] \\ -\left[\frac{\left[x_1\,K^*_{T1}(\ell)+x_2\,K^*_{T2}(\ell)\right]\left[x_1\,C^*_{pl1}(\ell)+x_2\,C^*_{p2}(\ell)\right]}{x_1\,E^*_{pl}(\ell)+x_2\,E^*_{p2}(\ell)}\right]\end{array}\right\}$$

Inspection shows that in each case the condition for simple additivity requires that the sum inside the brackets {……} vanishes. In the case of $C_{Vm}(mix;id)$ a sufficient condition (and most probably also necessary) is that $E^*_{p1}(\ell) = E^*_{p2}(\ell)\,[= E_{pm}(mix;id)]$ and that $K^*_{T1}(\ell) = K^*_{T2}(\ell)\,[= K_{Tm}(mix;id)]$ at a given T and p. In the case of $K_{Sm}(mix;id)$ the required conditions are that $E^*_{pl}(\ell) = E^*_{p2}(\ell)\,[= E_{pm}(\,mix;\,id)]$ and that $C^*_{p1}(\ell) = C^*_{p2}(\ell)\,[= C_{pm}(mix;id)]$ at a given T and p. But since $E_p = -(\partial S/\partial p)_T$ and $C_p = T\,(\partial S/\partial T)_p$, the condition can be restated as follows. Although molar entropies of liquid 1 and 2 may differ, they should have identical isobaric dependences on temperature and isothermal dependence on pressure. In the case of $E_{Sm}(mix;id)$ the three conditions are that $E^*_{p1}(\ell) = E^*_{p2}(\ell)\,[= E_{pm}(mix;id)]$, $K^*_{T1}(\ell) = K^*_{T2}(\ell)\,[= K_{Tm}(mix;id)]$, and $C^*_{pl}(\ell) = C^*_{p2}(\ell)\,[= C_{pm}(mix;id)]$.

If we extend the foregoing analysis to the variables isentropic compressibilities κ_S and isentropic expansibilities α_S we find that because $\kappa_S(mix;id) = K_{Sm}(mix;id)/V_m(mix;id)$, the condition described above for $K_{Sm}(\,mix;\,id)$ requires that $\kappa_S(mix;id)$ is given by the volume weighted sum of $\kappa^*_{sl}(\ell)$ and $\kappa^*_{S2}(\ell)$. Similarly we find that the three conditions described above in the context of $E_{Sm}(mix;id)$ is necessary in order that $\alpha_S(mix;id)$ is given by the volume weighted sum of $\alpha^*_{s1}(\ell)$ and $\alpha^*_{s2}(\ell)$.

The conditions described above are expressed in thermodynamic terms but we note that in no case can the properties of real pure liquids comply with these conditions. Nevertheless they provide useful pointers in the task of understanding the properties of real liquid mixtures. Even for a mixture prepared using $H_2O(\ell)$ and $D_2O(\ell)$, $C_{Vm}(mix;id)$ would depart from mole fraction additivity. Only for mixtures of ideal gases would the condition hold for $C_{Vm}(mix;id)$. Indeed for a monatomic gas the energy is entirely translational and $C_{pm} = (5/2)\backslash ldotR$.

Then $(\partial S_m/\partial T)_p = C_{pm}/T = (5/2)\,R/T$ for both pure gases and the mixture, a consequence of the Sackur-Tetrode equation for the molar entropy of ideal gases.

Footnote

[1] G. Douheret, M. I. Davis, J. C. R. Reis and M. J. Blandamer, Chem. Phys. Chem. Phys.,2001,**2**,148.

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1.18.5: Liquid Mixtures: Binary: Pseudo-Excess Properties

At defined T and p, a thermodynamic (molar) property P of an ideal binary liquid mixture (e.g. volume) can be expressed as a function of the mole fraction composition using equation (a).

$$\mathrm{P(mix;id)} = \mathrm{x_1\,P_1^*}(\ell) + \mathrm{x_2\,P_2^*}(\ell)$$

Here $\mathrm{P_1^*}(\ell)$ and $\mathrm{P_2^*}(\ell)$ are the properties of the two pure liquids at the same T and p. In many cases equation (a) is taken as a pattern on which to base a description of other properties of liquid mixtures; e.g. relative permitivities, surface tensions and viscosities. There is often no thermodynamic basis for this description although it has to be admitted that such an equation has an intuitively attractive form. In the next stage the difference between measured property $\mathrm{P(mix)}$ and $\mathrm{P(\ mix\ ;id)}$ leads to a defined pseudo-excess property. $\mathrm{P^E}$.

For the sake of completeness, the use of molar changes on mixing is recommended in the present context. Thus,

$$X_m(no-\mathrm{mix}) = x_1\,X_1^*(\ell) + x_2\,X_2^*(\ell)$$

Then by definition at common temperature and pressure,

$$\Delta_{\mathrm{mix}}\,X_m(\mathrm{mix}) = X_m(\mathrm{mix}) - X_m(no-mix)$$

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SECTION OVERVIEW

1.19: Perfect and Real Gases

Topic hierarchy

1.19.1: Perfect and Real Gases

1.19.2: Perfect Gas: The Gas Constant

1.19.3: Real Gases: Liquefaction of Gases

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1.19.1: Perfect and Real Gases

In a description of the properties of gases, the term 'perfect' means that there are no intermolecular forces, either attractive or repulsive. The equation of state for n_j moles of perfect gas j takes the following form where R is the Gas Constant, $8.314 JK^{-1}\ mol^{-1}$ [1].

$$p\,V_j = n_j\,R\,T$$

The chemical potential of a perfect gas μ_j^{id} at temperature T is related to pressure p_j using equation (b).

$$\mu_j^{id}\,(T, p_j) = \mu_j^{id}\,(T, p^0) + R\,T\,\ln\left(p_j/p^0\right)$$

Thus $\mu_j^{id}\,(T, p_j)$ is the chemical potential of gas j at pressure p_j whereas $\mu_j^{id}\,(T, p^0)$ is the corresponding chemical potential at the standard pressure p^0 [2].

The ratio (V_j/n_j) is the molar volume of gas j, V_{mj}. Equation (a) describing a perfect gas can be written as follows.

$$p_j^{id}\,V_{mj} = R\,T$$

No real gas is perfect at all temperatures and pressures although at high temperatures and low pressures the product $p_j\ V_{mj}$ is arithmetically almost equal to the product, $R\ T$. Generally however equation (c) does not describe real gases. The properties of real gases are described in several ways.

In one approach $\mu_j\,(T, p_j)$ is related to $\mu_j^{id}\,(T, p^0)$ using equation (d) where f_j is the fugacity.

$$\mu_j\,(T, p_j) = \mu_j\,(T, p^0) + R\,T\,\ln\left(f_j/p^0\right)$$

Thus

$$\text{limit}\,(p_j \to 0)\,f_j = p_j$$

Another approach uses virial coefficients [3]. Thus pressure p_j is related to molar volume \(\mathrm{V}_{\mathrm{mj}}\) using a power series in the term V_{mj}. Thus,

$$p_j = \frac{R\,T}{V_{mj}}\left[1 + \frac{B}{V_{mj}} + \frac{C}{V_{mj}^2} + \ldots\ldots\right]$$

In the event that a given gas is only slightly imperfect the terms C, D,…. are negligibly small. Then,

$$p_j = \frac{R\,T}{V_{mj}}\left[1 + \frac{B}{V_{mj}}\right]$$

At low temperatures B tends to be negative but at high temperatures B is positive.

Footnotes

[1] For equation (a),

$$\left[Nm^{-2}\right]\ \left[m^3\right] = [mol]\ \left[JK^{-1}\ mol^{-1}\right]\ [K]$$

where $[J] = [Nm]$

[2]

$$\mu_j^{id}\,(T, p_j) = \left[Jmol^{-1}\right] \quad R\,T = \left[Jmol^{-1}\ K^{-1}\right]\ [K] = \left[Jmol^{-1}\right]$$

[3] I. Prigogine and R. Defay, Chemical Thermodynamics, transl. D. H. Everett, Longmans Green, London, 1953, chapter 11.

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1.19.2: Perfect Gas: The Gas Constant

Throughout these Topics, the Gas Constant, symbol R, plays an important role. Here we examine how such an important quantity emerges [1].

An important concept in chemical thermodynamics is the perfect gas. In practice the properties of real gases differ from those of the perfect gas but the concept provides a useful basis for understanding the properties of real gases and by extension the properties of liquid mixtures and solutions. After all, nothing is perfect.

The starting point for the analysis is the following equation (see Topic 2500) for the change in thermodynamic energy of a closed system dU at temperature T, pressure p and affinity for spontaneous change A [1].

$$\mathrm{dU} = \mathrm{T\,dS} - \mathrm{p\,dV} - \mathrm{A\,d}\xi$$

Then for processes at equilibrium where A is zero,

$$\mathrm{dU} = \mathrm{T\,dS} - \mathrm{p\,dV}$$

For one mole of chemical substance j, equation (b) can be written in the following form.

$$\mathrm{dU_j} = \mathrm{T\,dS_j} - \mathrm{p\,dV_j}$$

Then,

$$\mathrm{dS_j} = \frac{\mathrm{dU_j} + \mathrm{p\,dVV_j}}{\mathrm{T}}$$

The molar isochoric heat capacity $\mathrm{C_{Vj}}$ describes the differential dependence of molar thermodynamic energy U_j on temperature at fixed volume. Thus

$$\mathrm{C_{Vj}} = (\partial \mathrm{U_j}/\partial \mathrm{T})_{\mathrm{V(j)}}$$

Using equation (d),

$$\mathrm{dS_j} = \frac{\mathrm{C_{v_j}}}{\mathrm{T}}\,\mathrm{dT} + \frac{\mathrm{p}}{\mathrm{T}}\,\mathrm{dV_j}$$

The latter equation emerges from an equation expressing the molar entropy of an ideal gas j as a function of the independent variables T and V_j. Thus,

$$\mathrm{S_j} = \mathrm{S_j}\,[\mathrm{T}, \mathrm{V_j}]$$

According to Joules Law [2]. The molar thermodynamic energy of a perfect gas depends only on temperature. Hence from equation (e) the molar isochoric heat capacity $\mathrm{C_{Vj}}$ is solely a function of temperature. Therefore equation (f) yields the following two important equations [3].

$$\left(\frac{\partial S_j}{\partial T}\right)_v = \frac{C_{v_j}}{T}$$

$$\left(\frac{\partial S_j}{\partial V}\right)_T = \frac{p}{T}$$

According to Boyles Law, the molar volume of gas j is inversely proportional to the pressure at fixed temperature. Thus

$$V_j = f(T)/p$$

Alternatively

$$\mathrm{p} = \mathrm{f(T)/V_j}$$

Hence using equation (i),

$$\left(\frac{\partial S_j}{\partial V}\right)_T = \frac{f(T)}{T V_j}$$

A calculus condition requires that

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)$$

In other words,

$$\frac{\partial\left(\mathrm{C_{vj}/T}\right)}{\partial \mathrm{V}} = \frac{\partial(\mathrm{p/T})}{\partial \mathrm{T}}$$

Or, using equation (k),

$$\frac{\partial\left(\mathrm{C_{v_j}/T}\right)}{\partial \mathrm{V}} = \frac{\partial\left[\mathrm{f(T)/T\,V_j}\right]}{\partial \mathrm{T}}$$

But the isochoric heat capacity $\mathrm{C_{Vj}}$ is independent of volume. Hence

$$\frac{\partial\left(\mathrm{C_{v_j}/T}\right)}{\partial \mathrm{V}} = 0$$

Then,

$$\frac{\partial\left[\mathrm{f(T)/T\,V_j}\right]}{\partial \mathrm{T}} = 0$$

In other words $\mathrm{[f(T)/T]}$ must be a constant, conventionally called the Gas Constant with symbol R. As the name implies R is a constant used to describe the properties of all gases [3]. We can therefore rewrite equation (k) as follows (recalling that $\mathrm{V_j}$ is the molar volume of a perfect gas) [4,5].

$$\mathrm{p\,V_j = R\,T}$$

The perfect gas is an artificial chemical substance having defined properties. The link with reality stems from the idea that the properties of real gases approach those of an ideal gas as the pressure is reduced.

In addition to the definition given by equation (q), the ideal gas is defined by the following equation which requires that the thermodynamic energy of an ideal gas is independent of volume, being nevertheless a function of temperature.

$$\mathrm{(\partial U_j/\partial V_j)_T} = 0$$

Footnotes

[1] I. Prigogine and R Defay, Chemical Thermodynamics, transl. D. H. Everett, Longmans Green, London, 1954, chapter X.

[2] Reference 1, page 116.

[3]

$$\mathrm{R} = 8.31450\ \mathrm{J\ K^{-1}\ mol^{-1}}$$
$$\mathrm{R = N_A\,k}$$

where $\mathrm{N_A}$ = Avogadro's constant and k = Boltzmann's constant

$$\mathrm{k} = 1.380658 \times 10^{-23}\ \mathrm{J\ K^{-1}}$$
$$\mathrm{N_A} = 6.0221367 \times 10^{23}\ \mathrm{mol^{-1}}$$

[4] G. N. Lewis and M. Randall, Thermodynamics, McGraw-Hill, 1923, page 63.

[5] P. W. Atkins, Concepts in Physical Chemistry, Oxford University Press, Oxford,1995.

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1.19.3: Real Gases: Liquefaction of Gases

In the nineteenth century a major theme in science concerned the properties of gases and their liquefaction. The challenge offered by the liquefaction of gases also prompted the development of thermodynamics and the production of low temperatures. Michael Faraday is noteworthy in this context. In 1823 Faraday had liquefied chlorine, ammonia and sulfur dioxide using a combination of pressure and low temperatures [1].

Based on the observation that the densities of liquids are higher than gases the expectation was that liquefaction of a given gas would follow application of high pressure. However this turned out not to be the case. For example, Newton showed that application of 2790 atmospheres ($\equiv 2.8 \times 10^8$ N m^{-2}) did not liquefy air. In 1877 Cailletet and Pictet working independently obtained a mist of oxygen by sudden expansion of gas compressed at 300 atmospheres ($\equiv 3 \times 10^7$ N m^{-2}) and cooled by $CO_2(s)$. However in developing the background to this subject we turn attention to the work of Joule.

Experiments by Joule

A gas, chemical substance j, is held in a closed system. The molar thermodynamic energy U_j is defined by equation (a) where V_j is the molar volume and T, the temperature.

$$\mathrm{U_j = U_j\,[T, V_j]}$$

The complete differential of equation (a) describes the change in $\mathrm{U_j}, \mathrm{dU_j}$, as a function of temperature and volume.

$$\mathrm{dU_j} = \left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{T}}\right)_{\mathrm{v}} \mathrm{dT} + \left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}} \mathrm{dV_j}$$

The molar isochoric heat capacity $\mathrm{C_{Vj}}$ is defined by equation (c).

$$\mathrm{C_{Vj}} = \left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

The first law of thermodynamics relates the change in U_j to the work done on the system w and heat q passing from the surroundings into the system. Thus,

$$\mathrm{dU_j = q + w}$$

Hence,

$$\mathrm{q} = \left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \mathrm{dT} + \left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}} \mathrm{dVV_j} - \mathrm{w}$$

The apparatus used by Joule comprised two linked vessels having equal volumes. A tube joining the two vessels included a tap. In an experiment, one vessel was filled with gas j at a known pressure whereas the second vessel was evacuated. When the tap was opened gas flowed into the second vessel, equalizing the pressure in the two vessels. By flowing into an evacuated vessel the gas did no work because there was no confining pressure; i.e. w = zero. The temperature of the gas in the containing vessel fell and that in the originally empty vessel rose by an equal amount. In other words dT for the two vessel system is zero. Hence

$$\left(\frac{\partial \mathrm{U}_j}{\partial \mathrm{T}}\right)_{\mathrm{V}} = 0$$

The clear hope was that the temperature would fall dramatically leading to liquefaction of the gas. In fact and with the benefit of hindsight the overall change in temperature dT was too small to be measured. More sophisticated apparatus would show that $\left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \neq 0$ because as the gas expands work is done against cohesive intermolecular interaction. It would only be zero for a perfect gas.

Experiments by Joule and Thomson [2,3]

In a series of famous experiments carried out in an English brewery, Joule and Thomson used an apparatus in which the gas under study passed through a porous plug from high to low pressures. The plug impeded the flow of the gas such that the pressure of the

gas on the high pressure side and the pressure of gas on the low pressure side remained constant. It was observed that the temperature of the gas decreased as a consequence of the work done by the gas against intermolecular cohesion.

A technological breakthrough was now made. A portion of the cooled gas was re-cycled to cool the gas on the input side. On passing through the plug the temperature of the gas fell to a lower temperature. As this process continues a stage was reached where a fraction of the gas is liquefied.

As noted above, the cooling emerges because work is done on expansion of the gases against intermolecular interaction. This is a quite general observation. When the pressure drops the mean intermolecular distance increases with the result that the temperature decreases. However there are exceptions to this generalisation. If the pressure is high the dominant intermolecular force is repulsion. Consequently when the pressure drops, work is done by the repulsive forces increasing the intermolecular distances thereby raising the temperature.

Footnotes

[1] The account given here is based on that given by N. K. Adam, Physical Chemistry, Oxford, The Clarendon Press, 1956, chapter III.

[2] Thomson ≡ Lord Kelvin

[3] J. P. Joule and W. Thomson, Proc. Roy. Soc.,1853,**143**,3457.

[4] G.N. Lewis and M. Randall, Thermodynamics, revised by K. S. Pitzer and L Brewer, McGraw-Hill, 2nd. edn.,1961, New York, pages 47-49.

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SECTION OVERVIEW

1.20: Surfactants

Topic hierarchy

1.20.1: Surface Phase: Gibbs Adsorption Isotherm

1.20.2: Surfactants and Micelles

1.20.3: Surfactants and Micelles: Non-Ionics

1.20.4: Surfactants and Miceles: Ionics

1.20.5: Surfactants and Micelles: Mixed

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1.20.1: Surface Phase: Gibbs Adsorption Isotherm

A given plane surface phase contains i-chemical substances having amounts n_j for each j-chemical substance. The plane surface phase is perturbed leading to a change in thermodynamic energy dU^σ where the symbol σ identifies the surface phase. Using the Master Equation as a guide we set down the corresponding fundamental equation for the plane surface phase [1-4].

$$\mathrm{dU}^\sigma = \mathrm{T\,dS}^\sigma - \mathrm{p\,dV}^\sigma + \gamma\,\mathrm{dA} + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mu_\mathrm{j}\,\mathrm{dn}_\mathrm{j}^\sigma$$

With reference to equation (a), $\mathrm{T},\ \mathrm{p}, \gamma$ and μ_j are intensive variables whereas $\mathrm{U},\ \mathrm{S},\ \mathrm{V},\ \mathrm{A}$ and n_j are extensive variables. We integrate equation (a) to yield equation (b).

$$\mathrm{U}^\sigma = \mathrm{T\,S}^\sigma - \mathrm{p\,V}^\sigma + \gamma\,\mathrm{A} + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mu_\mathrm{j}\,\mathrm{n}_\mathrm{j}^\sigma$$

The general differential of equation (b) is equation (c).

$$\mathrm{dU}^\sigma = \mathrm{T\,dS}^\sigma + \mathrm{S}^\sigma\,\mathrm{dT} - \mathrm{p\,dV}^\sigma - \mathrm{V}^\sigma\,\mathrm{dp} + \gamma\,\mathrm{dA} + \mathrm{A\,d}\gamma + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mu_\mathrm{j}\,\mathrm{dn}_\mathrm{j}^\sigma + \sum_{\mathrm{j=1}}^{\mathrm{o}} \mathrm{n}_\mathrm{j}^\sigma\,\mathrm{d}\mu_\mathrm{j}$$

Using equations (a) and (c).

$$0 = \mathrm{S}^\sigma\,\mathrm{dT} - \mathrm{V}^\sigma\,\mathrm{dp} + \mathrm{A\,d}\gamma + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{n}_\mathrm{j}^\sigma\,\mathrm{d}\mu_\mathrm{j}$$

Hence for a surface phase σ at fixed T and p,

$$0 = \mathrm{A\,d}\gamma + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{n}_\mathrm{j}^\sigma\,\mathrm{d}\mu_\mathrm{j}$$

We restrict attention to two component systems, comprising components labelled 1 and 2 wherein there are two phases α and β. In practice the boundary between phases α and β comprises a region across which the compositions of small sample volumes change from pure i to pure j. We imagine that the boundary layer can be replaced by a surface. For component j, Γ_j is the amount of chemical substance j adsorbed per unit area; i.e. the surface concentration expressed in molm^{-2}. Then,

$$0 = \mathrm{d}\gamma + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \Gamma_\mathrm{j}\,\mathrm{d}\mu_\mathrm{j}$$

Consider the case of a system prepared using two chemical substances, 1 and 2. We set the interphase between the two phases by a mathematical plane where Γ_1 is zero. Then

$$\Gamma_2 = -\mathrm{d}\gamma/\mathrm{d}\mu_2$$

The definition based on Γ_1 defines the surface excess per unit area of the surface separating the two phases.

Chemical substance 1 is the solvent (e.g. water) and chemical substance 2 is the solute. The surface divides the liquid and vapor phases. Equation (g) describes the surface excess of the solute. We assume that the surface and bulk aqueous phases are in (thermodynamic) equilibrium. Moreover we assume that the thermodynamic properties of the solutions are ideal. Then in terms of the concentration scale (where $\mathrm{c}_r = 1\ \mathrm{moldm}^{-3}$),

$$\mu_2(aq) = \mu_2^0(aq) + RT\,\ln\left(c_2/c_r\right)$$

Then,

$$\mathrm{d}\mu_2(\mathrm{aq}) = \mathrm{R\,T\,d\ln}\left(\mathrm{c}_2/\mathrm{c}_\mathrm{r}\right)$$

Hence,

$$\Gamma_2 = -\frac{1}{R\,T}\,\frac{d\gamma}{d\ln(c_2/c_r)}$$

Equation (j) is the 'Gibbs adsorption equation' for a two-component system using the Gibbs definition of surface excess. The validity of the Gibbs treatment was confirmed in 1932 by McBain who used an automated fast knife to remove a layer between 5 and 1 mm thick from the surface of a solution [5]. The compositions of this layer and the solution were than analyzed. As N. K. Adam comments [1] 'in every case so far examined', the measured adsorption agreed with that predicted by Equation (j).

If γ decreases with increase in c_2, Γ_2 is positive as is the case for organic solutes then these solutes are positively adsorbed at the air-water interface. The reverse pattern is observed for salt solutions.

Footnotes

[1] N. K. Adam, The Physics and Chemistry of Surfaces, Dover, New York, 1968; a corrected version of the third edition was published in 1941 by Oxford University Press.

[2] N. K. Adam, Physical Chemistry, Oxford, 1956, chapter XVII.

[3] S. E. Glasstone, Physical Chemistry, MacMillan, London, 1948, chapter XIV. As forcefully expressed to undergraduates, N. K. Adam did not like the symbols used in this reference.

[4] G. N. Lewis and M. Randall, Thermodynamics, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 2nd edn., 1961, chapter 29.

[5] J. W. McBain and C. W. Humphreys, J. Phys.Chem.,1932,**36**,300.

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1.20.2: Surfactants and Micelles

'Nonsense, McBain'. The story is told that with these words an eminent scientist, chairman of a meeting of the Royal Society in London in the early 20th Century, reacted to the proposal by J. W. McBain that surfactants [= **surf**ace **act**ive **a**g**ents**] might aggregate in aqueous solution [1]. Subsequent events confirmed that the nub of McBain's model is correct.

The enormous industry based on 'soaps' and detergents [2] prompts intensive studies of these complicated systems, supported by monographs [3-5] and detailed reviews [6-11].

In the context of aqueous solutions, surfactant molecules are amphipathic meaning that the solutes have dual characteristics : amphi ≡ dual and pathi ≡ sympathy. These dual characteristics emerge because a solute molecule contains both hydrophobic and hydrophilic parts. The subject is complicated because there is no general agreement concerning the nature-structure of these solute aggregates in aqueous solutions. Amphipathic molecules are broadly classified as either ionic or non-polar. Ionic surfactants are typified by salts such as sodium dodecylsulfate ($C_{12}H_{25}OSO_3^-\ Na^+$) and hexyltrimethylammonium bromide ($C_{16}H_{33}N^+\ Me_3Br^-$; CTAB). Non-ionic surfactants are typified by those based on ethylene oxide; e.g. hexaethylene glycol dodecylether, ($C_{16}H_{25}\,(OCH_2CH)_6\,OH$).

When small amounts of a given surfactant are gradually added to a given volume of water (ℓ), the properties of the aqueous solutions are unexceptional until the concentration of the surfactant exceeds a characteristic concentration of surfactant (at defined T and p) called the critical micellar concentration, cmc. At this point further added surfactant exists in solution as aggregates of generally 20 to 100 monomers, which are called micelles. The formation of micelles is often signalled by a change in the pattern of the dependence of a given property P of a solution on surfactant concentration. The property can be surface tension, molar conductance of an ionic surfactant, uv-visible absorption spectra of water soluble dyes (or, an iron complex [12]). When more surfactant is added, the micelles cluster to form more complicated aggregates [13].

Micelles are not formed by the gradual association of monomers, forming dimers, trimers…..[14] . Rather micelles are examples of organized structures spontaneously formed by simple molecules [15]. A quoted aggregation number is not a stoichiometric number. The quoted number (e.g. approx. 90 for CTAB at $298\ K$) is taken as an 'average' over the micelles in a given system.

In terms of the structure of micelles in aqueous solutions, key questions centre on

1. the extent to which water penetrates into a micelle, and
2. the organization of alkyl chains in a given micelle [16].

The two questions are linked by the question – to what extent does the terminal group in, for example, the hexadecyl chains of CTAB come into contact with the aqueous solution? If the answer is 'never', micelles have a structure in which there is a well organized hydrophobic core. If the answer is 'frequently' the micelles are very dynamic assemblies with continuous changes in organization/structure. We do not become involved in this debate. However we note that there is such a debate over what precisely the thermodynamic analysis is asked to describe.

Description of micellar-surfactant systems emerges from the Phase Rule. The number of phases = 3; vapor, aqueous solution and micelle. The number of components = 2; water and surfactant. Hence having defined the temperature, the remaining intensive variables are defined; i.e. vapor pressure, mole fraction of surfactant monomer in aqueous solution, and mole fraction of surfactant in micellar phase.

The starting point for a thermodynamic analysis is the assumption of an equilibrium between surfactant monomers and micelles in solution (at defined T and p). A key feature of these systems is that above the cmc when more surfactant is added the concentration of monomers remains essentially constant, the added surfactant existing in micellar form. Two models for micelle formation are discussed;

i. phase equilibrium [17], and
ii. closed association model, often called the mass-action model.

Here we assume that the closed system containing solvent and surfactant is at equilibrium at defined T and p. Each system is at a unique minimum in Gibbs energy. The system is at ambient pressure, which for our purposes is effectively the standard pressure p^0. We characterize micelle formation using thermodynamic variables describing monomers and micelles. Then $\Delta_{mic}\,G^0$ is the standard

Gibbs energy of micelle formation which is dependent on temperature. The latter dependence is characterized by the standard enthalpy of micelle formation, $\Delta_{\mathrm{mic}} H^0$, where,

$$\Delta_{\mathrm{mic}}\ \mathrm{G}^0 = \Delta_{\mathrm{mic}}\ \mathrm{H}^0 - \mathrm{T}\ \Delta_{\mathrm{mic}}\ \mathrm{S}^0$$

Clearly the definition of $\Delta_{\mathrm{mic}}\ \mathrm{G}^0$ is directly associated with the definition of standard states for both the simple salt in solution and the micelles in the aqueous system. These thermodynamic variables together with aggregation numbers are extensively documented [18].

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1.20.3: Surfactants and Micelles: Non-Ionics

The properties of aqueous solutions containing non-ionic surfactants [1-6] can be described using two models.

Model Phase Equilibrium: Dry Micelle

We envisage a non-ionic surfactant X. When chemical substance X is added to $\mathrm{n_1}$ moles of water (at fixed T and p), solute X exists as a simple solute $\mathrm{X(aq)}$ until the concentration of solute X, $\mathrm{c_X}$ reaches a characteristic concentration $\mathrm{cmc_X}$ when a trace amount of the micellar phase appears. Each micelle comprises n molecules of surfactant X. The equilibrium between monomer surfactant \(\mathrm{X}(\aq) and surfactant in the micelles is described by the following equation.

$$\mu_{\mathrm{X}}^{\mathrm{eq}}(\mathrm{aq}) = \mu_{\mathrm{X}}^{*}(\mathrm{mic})$$

If $\mathrm{X(aq)}$ is a typical neutral solute in aqueous solution $\mu_{\mathrm{x}}^{\mathrm{eq}}(\mathrm{aq})$ is related to the cmc of $\mathrm{X(aq)}$ in solution at the point where only a trace amount of micellar phase exists. Hence,

$$\mu_{\mathrm{X}}^{0}(\mathrm{aq;c-scale}) + \mathrm{R\,T\,ln\,(cmc\,y_X/c_r)} = \mu_{\mathrm{X}}^{*}(\mathrm{mic})$$

Here $\mathrm{y_X}$ is the solute activity coefficient for $\mathrm{X(aq)}$ taking account of solute-solute interactions in the aqueous solution. Therefore, by definition,

$$\Delta_{\mathrm{mic}}\,\mathrm{G^0(aq)} = -\mathrm{R\,T\,ln\,(K_{mic}^0)} = \mu_{\mathrm{X}}^{*}(\mathrm{mic}) - \mu_{\mathrm{x}}^{0}(\mathrm{aq;c-\ scale\ })$$

Equilibrium constant $\mathrm{K_{mic}^0}$ describes the phase equilibrium involving surfactant X in aqueous solution and micellar phase.

$$\Delta_{\mathrm{mic}}\,\mathrm{G^0(aq)} = -\mathrm{R\,T\,ln\,(K_{mic}^0)} = \mathrm{R\,T\,ln\,(cmc\,y_X/c_r)}$$

If $\mathrm{X(aq)}$ is a neutral solute and the cmc is low, a useful approximation sets $\mathrm{y_X}$ at unity. Therefore $\Delta_{\mathrm{mic}}\,\mathrm{G^0(aq)}$ is the standard increase in Gibbs energy when one mole of surfactant $\mathrm{X(aq)}$ forms one mole of X in the micellar phase. Combination of equations (c) and (d) yields equation (e).

$$\mathrm{K_{mic}^0} = (\mathrm{cmc/c_r})^{-1}$$

Here $\mathrm{K_{mic}^0}$ describes the equilibrium between surfactant in the micellar phase and the aqueous solution. A famous equation suggested by Harkin relates the cmc to the number of carbon atoms in the alkyl chain, $\mathrm{n_C}$; equation (f)

$$\mathrm{log\,(cmc/c_r)} = \mathrm{A - B\,n_C}$$

With equation (e),

$$\mathrm{log\,(K_{mic}^0)} = A - (B\,n_C)$$

The above analysis is also used for ionic surfactants if it can be assumed the degree of counter ion binding by the micelles is small, the thermodynamic properties of the solution are ideal and the aggregation number is high.

Non-Ionic Surfactant: Phase Equilibrium: Wet Micelle

The aqueous phase comprises an aqueous solution of solute X, $\mathrm{X(aq)}$. The micellar phase comprises both water and surfactant X such that the mole fraction of surfactant in the micellar phase equals $\mathbf{x}_{\mathrm{X}}^{\mathrm{eq}}$. We treat the micellar phase using the procedures used to describe the properties of a binary liquid mixture. For the micellar phase the chemical potential of X is given by the following equation.

$$\mu_{\mathrm{x}}(\mathrm{mic}) = \mu_{\mathrm{x}}^{*}(\ \mathrm{mic}\ ) + \mathrm{R\,T\,ln\,(x_x\,f_x)^{eq}}$$

where

$$\mathrm{limit}\,(x_x \to 1)\,f_x = 1 \text{ at all T and p}$$

But at equilibrium for a system containing a trace of the micellar phase,

$$\mu_{\mathrm{x}}^{\mathrm{eq}}(\mathrm{mic}) = \mu_{\mathrm{x}}^{\mathrm{eq}}(\mathrm{aq})$$

Then,

$$\mu_X^{\circ}(\text{ mic }) + R\,T\,\ln\left(x_X\,f_X\right)^{eq} = \mu_X^0(aq) + R\,T\,\ln\left(cmc_x\,y_X/c_r\right)$$

By definition

$$\Delta_{mic}\,G^0 = -R\,T\,\ln\left(K_{mic}^0\right) = \mu_x^*(mic) - \mu_x^0(aq)$$

Then,

$$K_{mic}^0 = \left[x_X\,f_X\right]^{eq} / \left[cmc/c_r\right]$$

If the micelle is only 'damp' rather than wet , a reasonable assumption sets f_X equal to unity although it is not obvious how x_X might be determined.

Non-Ionic Surfactant: Mass Action Model: Dry Micelle

Micelle formation is described as an equilibrium between $X(aq)$ as a solute in aqueous solution and a micellar aggregate in aqueous solution formed by n molecules of the monomer $X(aq)$. Then at the point where micelles are first formed, the following equilibrium is established.

$$nX(aq) \Leftrightarrow X_n(aq)$$

The total amount of surfactant in the system equals $N(X;aq) + n\,N\left(X_n;mic\right)$ where $N(X;aq)$ is the amount of monomer surfactant and where $N\left(X_n;mic\right)$ is the total amount of micelles , each micelle containing n surfactant molecules. But for the micellar aggregate $X_n(aq)$ treated as a single solute,

$$\mu\left(X_n;aq\right) = \mu^0\left(X_n;aq\right) + R\,T\,\ln\left[c\left(X_n\right)\,y\left(X_n\right)/c_r\right]$$

Here $c\left(X_n\right)\left[= N\left(X_n;aq\right)/V\right.$ where V is the volume of the system] is the concentration of micelles in the system, activity coefficient $y\left(X_n\right)$.The latter can be assumed to be unity if there are no micelle-micelle interactions and no micelle-monomer interactions in the aqueous system. Although this approach seems similar to that used to describe chemical equilibria, the procedure has problems in the context of determining $c\left(X_n\right)$.

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1.20.4: Surfactants and Miceles: Ionics

An intense debate concerns the structure of micelles, particularly those formed by ionic surfactants such as SDS and CTAB. It seems generally agreed that micelles are essentially spherical in shape. The polar head groups (e.g. $-N^+Me_3$) are at the surface of each micelle, having strong interactions with the surrounding solvent. In close proximity in the Stern layer are counterions (e.g. bromide ions in the case of CTAB); the aggregation number n describes the number of cations which form each micelle. The total charge on the micelle is determined the aggregation number and a quantity β, the latter being the fraction of charge of aggregated ions forming the micelle neutralized by the micelle bound counter ions. The remaining fraction of counter ions exists as 'free' ions in aqueous solution. Both $mathrmn$ and β are characteristic of a given surfactant system, and are obtained from analysis of experimental data [1]. The properties of ionic surfactants have been extensively studied [2-14]. Here we examine four thermodynamic descriptions of these systems.

Ionic Surfactant:1:1 salt: Phase Equilibrium: Dry Neutral Micelle

We consider a dilute aqueous solution of an ionic surfactant; e.g. AM^+Br^-. As more surfactant is added a trace amount of micelles appear in the solution when the concentration of surfactant just exceeds the cmc. The trace amount of surfactant is present as micelles constituting a micellar phase. At defined T and p, the following equilibrium is established in the case of the model surfactant AM^+Br^-;

$$AM^+Br^-(aq) \Leftrightarrow AM^+Br^-(mic)$$

Then,

$$\mu^{cq}\left[AM^+Br^-(aq)\right] = \mu^{cq}\left[AM^+Br^-(mic)\right]$$

We assume that the micelles carry no charge. The chemical potential of the surfactant in aqueous solution is related to the cmc using the following equation where $y_\pm$ is the mean ionic activity coefficient. We set $\mu^{eq}\left[AM^+Br^-(mic)\right]$ equal to the chemical potential of the surfactant in the pure micellar state, $\mu^*\left[AM^+Br^-(mic)\right]$.

$$\mu^0\left(AM^+Br^-; aq; c-scale\right) + 2\,R\,T\,\ln\left(cmc\,y_\pm/c_r\right) = \mu^*\left(AM^+Br^-; \text{micellar phase}\right)$$

Here $\mu^0\left(AM^+Br^-; aq; c-\text{scale}\right)$ is the chemical potential of the salt AM^+Br^- in aqueous solution at unit concentration where the properties of the salt are ideal. Thus $y_\pm$ describes the role of ion-ion interactions in the solution having salt concentration cmc. Because the model states that there is only a trace amount of micelles in the system, we do not take account of salt-micelle interactions. Then

$$\Delta_{mic}\,G^0 = \mu^*\left(\text{micellar phase}; AM^+Br^-\right) - \mu^0\left(AM^+Br^-; aq; c-\text{scale}\right)$$

Hence,

$$\Delta_{mic}\,G^0(aq; c-\text{scale}) = 2\,R\,T\,\ln\left(cmc\,y_\pm/c_r\right)$$

If the salt concentration in the aqueous solution at the cmc is quite low, a useful assumption sets $y_\pm$ equal to unity. Then,

$$\Delta_{mic}\,G^0(aq; c-scale) = 2\,R\,T\,\ln\left(cmc/c_r\right)$$

The latter equation leads to the calculation of the standard increase in Gibbs energy when one mole of salt AM^+Br^- passes from the ideal solution, concentration $1 moldm^{-3}$ to the micellar phase.

There is a modest problem with the latter equation which can raise conceptual problems. As normally stated the cmc for a given salt is expressed using the unit '$moldm^{-3}$' so that $c_r = 1\ moldm^{-3}$. This means that when $cmc > 1\ moldm^{-3}$, $\Delta_{mic}G^0(aq; c-\text{scale})$ is positive. For solutes where $cmc < 1\ moldm^{-3}$, the derived quantity is negative.

Another approach expresses the cmc using the mole fractions, cmx such that equation (c) is written as follows.

$$\mu^0\left(AM^+Br^-; aq; x-scale\right) + 2\,R\,T\,\ln\left(cmx\,f^*_\pm\right) = \mu^*\left(AM^+Br^-; \text{micellar phase}\right)$$

Here $\mu^0\left(\mathrm{AM^+Br^-;aq;x-\ scale\ }\right)$ is the chemical potential of the salt $\mathrm{AM^+Br^-}$ in an ideal solution where the (asymmetric) activity coefficient $\mathrm{f_\pm^*=1.0}$ and $\mathrm{cmx=1.0.}$.

By definition $\mathrm{limit}\left[x\left(\mathrm{AM^+Br^-}\right)\rightarrow 0\right]\mathrm{f_\pm^*=1.0\ at\ all\ T\ and\ p.}\}$ The analogue of equation (f) takes the following form.

$$\Delta_{\mathrm{mic}}\,\mathrm{G^0(aq;x-\ scale\ )=2\,R\,T\ ln(cmx)}$$

Because cmx is always less than unity, $\Delta_{\mathrm{mic}}\,G^0(aq;x-\ \mathrm{scale}\ )$ is always negative. It is important in these calculations to note the definitions of reference and standard states for solutes and micelles otherwise false conclusions can be drawn [14]. The analysis proceeds to use the Gibbs-Helmholtz equation. Hence,

$$\Delta_{\mathrm{mic}}\,\mathrm{H^0(aq;x-\ scale\ )=-2\,R\,T^2\left\{\partial\ln(cmx)/\partial T\right\}_p}$$

The term $\left\{\partial\ln(\mathrm{cmx})/\partial\mathrm{T_P}\right.$ is conveniently obtained by expressing the dependence of cmx on temperature using the following polynomial.

$$\ln(cmx)=a_1+a_2\,T+a_3\,T^2+...$$

Equation (h) is straightforward, the stoichiometric factor '2' emerging from the fact that each mole of salt $\mathrm{AM^+Br^-}$ produces on complete dissociation 2 moles of ions. A key assumption in this analysis is that the micelles carry no electric charge. In other words a micelle is formed by n moles of cation $\mathrm{AM^+}$, n moles of counter ions $\mathrm{Br^-}$ being bound within the Stern layer such that the charge on each micelle is zero. This model is a little unrealistic.

Ionic Surfactant: 1:1 salt: Phase Equilibrium: Dry Charged Micelle

A cationic surfactant $\mathrm{AM^+Br^-}$ in aqueous solution forms micelles when n cations come together to form a micellar phase. Bearing in mind that n might be greater than 20, the idea that there exists micro-phases of macro-cations in a system with an electric charge at least +20 is not attractive. In practice the charge is partially neutralised by bromide ions in the Stern layer. The quantity β refers to the fraction of counter ions bound to cations. Thus the formal charge number on each micelle is $[n\ (1-\beta)]$. In the model developed here we represent the formation of the micro-phase comprising the micelles as follows where n is the number of cation monomers which cluster, the remaining bromide ions being present in the aqueous solution (phase).

$$\begin{aligned}&\mathrm{nAM^+(aq)+n\,(1-\beta+\beta)Br^-(aq)}\\&\qquad\Leftrightarrow\left[\mathrm{nAM^+n\,\beta Br^-}\right]^{\mathrm{n\,(1-\beta)}}\mathrm{(mic)+n\,(1-\beta)Br^-(aq)}\end{aligned}$$

We re-express this equilibrium in terms of equilibrium chemical potentials for a system at fixed T and p.

$$\begin{aligned}&\mathrm{n}\,\mu^{\mathrm{eq}}\left(\mathrm{AM^+;aq}\right)+\mathrm{n}\,(1-\beta+\beta)\,\mu^{\mathrm{eq}}\left(\mathrm{Br^-;aq}\right)\\&=\mu^{\mathrm{eq}}\left\{\left[\mathrm{nAM^+n}\,\beta\mathrm{Br^-}\right]^{\mathrm{n}(1-\beta)};\ \mathrm{micelle}\ \right\}+\mathrm{n}\,(1-\beta)\mu^{\mathrm{cq}}\left(\mathrm{Br^-;aq}\right)\end{aligned}$$

We define the chemical potential of the micelle microphase which contains 1 mole of $\mathrm{AM^+}$. This is a key extrathermodynamic step. We also describe the micelle as a pure 'phase'.

$$\begin{aligned}&\mu^{\mathrm{eq}}\left\{\left[\mathrm{AM^+}\beta\mathrm{Br^*}\right]^{(1-\beta)};\ \mathrm{micelle}\ \right\}\\&\qquad=\mu^{\mathrm{cq}}\left\{\left[\mathrm{nAM^+n}\,\beta\mathrm{Br^-}\right]^{\mathrm{n}(1-\beta)};\ \mathrm{micelle}\ \right\}/\mathrm{n}\end{aligned}$$

Hence,

$$\begin{aligned}&\mu^{\mathrm{eq}}\left(\mathrm{AM^+;aq}\right)+\mu^{\mathrm{eq}}\left(\mathrm{Br^-;aq}\right)\\&=\mu^*\left\{\left[\mathrm{AM^+}\beta\mathrm{Br^*}\right]^{(1-\beta)};\ \mathrm{micelle}\ \right\}+(1-\beta)\mu^{\mathrm{eq}}\left(\mathrm{Br^-;aq}\right)\end{aligned}$$

Or,

$$\begin{aligned}&\mu^{\mathrm{cq}}\left(\mathrm{AM^+Br^{-1};aq}\right)=\\&\mu^{\mathrm{eq}}\left\{\left[\mathrm{AM^+}\beta\mathrm{Br^-}\right]^{(1-\beta)};\ \mathrm{micelle}\right\}\ +(1-\beta)\mu^{\mathrm{cq}}\left(\mathrm{Br^-;aq}\right)\end{aligned}$$

The term $\mu^{\mathfrak{T}}\left(\mathrm{AM^+Br^{-1};aq}\right)$ is the equilibrium chemical potential of a 1:1 salt in solution at the cmc. The term $\mu^{\mathrm{eq}}\left(\mathrm{Br^-;aq}\right)$ is the equilibrium chemical potential of the bromide ion in the solution at the cmc of the surfactant. In any event the system is electrically

neutral.

$$\mu^0\left(\mathrm{AM^+Br^{-1}; aq}\right) + 2\,\mathrm{R\,T}\,\ln\left[\mathrm{cmc\,y\left(AM^+Br^-\right)/c_r}\right]$$
$$= \mu^*\left\{\left[\mathrm{AM^+}\beta\mathrm{Br^*}\right]^{(1-\beta)};\ \mathrm{micelle}\right\}$$
$$+ (1-\beta)\left\{\mu^0\left(\mathrm{Br^-; aq}\right) + \mathrm{R\,T}\,\ln\left[\mathrm{cmc\,y\left(Br^-\right)/c_r}\right]\right\}$$

By definition,

$$\Delta_{\mathrm{mic}}\,\mathrm{G}^0 = \mu^*\left\{\left[\mathrm{AM^+}\beta\mathrm{Br^*}\right]^{(1-\beta)};\ \mathrm{micelle}\right\}$$
$$+ (1-\beta)\,\mu^0\left(\mathrm{Br^-; aq}\right) - \mu^0\left(\mathrm{AM^+Br^{-1}; aq}\right)$$

Assuming both $\mathrm{y\left(AM^+Br^-\right)}$ and $\mathrm{y\left(Br^-\right)}$ are unity,

$$\Delta_{\mathrm{mic}}\,\mathrm{G}^0 = 2\,\mathrm{R\,T}\,\ln\left[\mathrm{cmc/c_r}\right] - (1-\beta)\,\mathrm{R\,T}\,\ln\left[\mathrm{cmc/c_r}\right]$$

or

$$\Delta_{\mathrm{mic}}\,\mathrm{G}^0 = (1+\beta)\,\mathrm{R\,T}\,\ln\left[\mathrm{cmc/c_r}\right]$$

The latter equation closely resembles that for non-ionic surfactants for which β is unity. For ionic surfactants it is not justified to assume that β is also unity.

Ionic Surfactant: 1:1 salt: Dry Charged Micelle:Mixed Salt Solutions

As more ionic surfactant is added to a solution having the concentration of surfactant equal to the cmc, so the solution increasingly resembles a mixed salt solution, simple salt, charged micelles and counter ions. Analysis of the properties of such solutions was described by Burchfield and Woolley [2-5]. We might develop the analysis from equation (k). An advantage of writing the equation in this form stems from the observation that both sides of the equation describe an electrically neutral system. Woolley and co--workers [4,5] prefer a form which removes a contribution $\mathrm{n}\,(1-\beta)\mathrm{Br^-(aq)}$ from each side of equation (k).

$$\mathrm{nAM^+(aq)} + \mathrm{n}\,\beta\mathrm{Br^-(aq)} \Leftrightarrow \left[\mathrm{nAM^+n}\,\beta\mathrm{Br^-}\right]^{\mathrm{a}\,(1-\beta)}\mathrm{(aq)}$$

Nevertheless one might argue that equation (k) does have the merit in comparing two salts whereas equation (t) describes the links between three ions. In terms of equation (k) , there are two salts in solution.

I. $\mathrm{AM^+Br^-}$ where $v_+ = 1, v_- = 1, v = 2, Q = \left(v_+^{v+}\,v_-^{v-}\right)^{1/v} = 1, y_\pm^v = y_+^{v+}\,y_-^{v-},$ or $y_\pm^2 = y_+\,y_-$ But

$$\mu\left(\mathrm{AM^+Br^-}\right) =$$
$$\mu^0\left(\mathrm{AM^+Br^-}\right) + 2\,\mathrm{R\,T}\,\ln\left(\mathrm{c\left(AM^+Br^-\right)\,y_\pm\left(AM^+Br^-\right)/c_r}\right)$$

II. For the micellar salt, $\left[\mathrm{nAM^+n}\,\beta\mathrm{Br^-}\right]^{\mathrm{n}\,(1-\beta)}\,\mathrm{n}\,(1-\beta)\mathrm{Brr^-}$
$\mathrm{v_+} = 1, \mathrm{v_-} = \mathrm{n}\,(1-\beta)$, and $v = n\,(1-\beta)+1$ and $\mathrm{Q^{n(1-\beta)+1}} = \left[1\left\{\mathrm{n}\,(1-\beta)\right\}^{\mathrm{n}(1-\beta)}\right]$ with $\mathrm{y_\pm^{n\,(1-\beta)+1}} = \mathrm{y_+^1\,y_-^{n\,(1-\beta)}}$
Then,

$$\mu(\ \mathrm{mic.\ salt}\ )$$
$$= \mu^0\ (\mathrm{mic.\ salt}\ ) + [n\,(1-\beta)+1]\,RT\,\ln\left[Q\,c(\ \mathrm{mic.salt}\ )\,y_\pm/c_r\right]$$

At equilibrium,

$$\mathrm{n}\,\mu^{\mathrm{eq}}\left(\mathrm{AM^+Br^-; aq}\right) = \mu^{\mathrm{eq}}(\ \mathrm{mic.\ salt;\ aq}\ )$$

Hence,

$$\Delta_{\mathrm{mics\ slt}}\,\mathrm{G}^0 = -\mathrm{R\,T}\,\ln\left(\mathrm{K_0}\right) = \mu^0(\ \mathrm{mic.salt}\ ) - \mathrm{n}\,\mu^0\left(\mathrm{AM^+Br^-}\right)$$

The total concentration of salt ctot in the system is given by equation (y).

$$\mathrm{ctot\left(AM^+Br^-; system\ \right) = n\,c(\ ch\ arg\ ed\ micelles\ ) + c\left(AM^+Br^-; aq\right)}$$

The analysis makes no explicit reference to a cmc. Instead the micellar system is described as a mixed salt solution. Application of these equations requires careful computer –based curve fitting for multi-parametric equations. The latter include equations relating

mean ionic activity coefficients for salts to the composition of a given solution. A shielding factor δ was use by Burchfield and Woolley to reduce the impact of micellar charge of the cationic micelles on calculated ionic strength [2]. Thus the effective charge on the cationic micelles was written as $n\,(1-\beta)\,\delta$ where δ is approx. 0.5.

Ionic Surfactant: Mass Action Model

In general terms the equilibrium between surfactant monomers Z^{+}, counter anions X^{-} and micelles M can be represented by the following equation.

$$\mathrm{n}Z^{+}(\mathrm{aq}) + \mathrm{mXX}^{-}(\mathrm{aq}) \Leftrightarrow \mathrm{M}^{(\mathrm{n-m})+}(\mathrm{aq})$$

Then in terms of the mass action model, the concentration equilibrium constant,

$$\mathrm{K}_{\mathrm{c}}^{0} = \left[\mathrm{M}^{(\mathrm{n-m})+}\right] / \left\{\left[\mathrm{Z}^{+}\right]^{\mathrm{n}}\,\left[\mathrm{X}^{-}\right]^{\mathrm{m}}\right\}$$

By definition,

$$\Delta_{\mathrm{mic}}\,\mathrm{G}^{0} = -(\mathrm{n})^{-1}\,\mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{K}_{\mathrm{c}}^{0}\right)$$

Then,

$$\Delta_{\mathrm{mic}}\,\mathrm{G}^{0}/(\mathrm{R}\,\mathrm{T}) = -(\mathrm{n})^{-1}\,\ln\left[\mathrm{M}^{(\mathrm{n-m})+}\right] + \ln\left[\mathrm{Z}^{+}\right] + (\mathrm{m}/\mathrm{n})\,\ln\left[\mathrm{X}^{-}\right]$$

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1.20.5: Surfactants and Micelles: Mixed

In many industrial and commercial applications, mixed surfactant systems are used [1]. An extensive literature examines the properties of these systems [2-8].

A given aqueous solution contains two surfactants X and Y at temperature T and pressure p. The critical micellar concentrations are $\mathrm{cmc}_{\mathrm{X}}^{0}$ and $\mathrm{cmc}_{\mathrm{Y}}^{0}$. For a solution containing both surfactants X and Y, the critical micellar concentration of the mixed surfactant is cmc(mix). Here we use a pseudo-separate phase model for the micelles. The system under consideration comprises $\mathrm{n}_{\mathrm{X}}^{0}$ and $\mathrm{n}_{\mathrm{Y}}^{0}$ moles of the two surfactants. [Here the superscript 'zero' refers to the composition of the solution as prepared using the two pure surfactants.] A property r is the ratio of the concentration of surfactant Y to the total concentration of the two surfactants in the solution. Thus,

$$\mathrm{r} = \frac{\mathrm{n}_{\mathrm{Y}}^{0}}{\mathrm{n}_{\mathrm{X}}^{0} + \mathrm{n}_{\mathrm{Y}}^{0}} = \frac{\mathrm{c}_{\mathrm{Y}}^{0}}{\mathrm{c}_{\mathrm{X}}^{0} + \mathrm{c}_{\mathrm{Y}}^{0}}$$

Here $\mathrm{c}_{\mathrm{X}}^{0}$ and $\mathrm{c}_{\mathrm{Y}}^{0}$ are the concentrations of the two surfactants in solution. We define a model system where cmc(mix) is a linear function of the property r; equation (b).

$$cmc(\mathrm{mix}) = \left(\mathrm{cmc}_{\mathrm{Y}}^{0} - \mathrm{cmc}_{\mathrm{X}}^{0}\right)\,\mathrm{r} + \mathrm{cmc}_{\mathrm{X}}^{0}$$

Or,

$$\mathrm{cmc(mix)} = \mathrm{r}\,\mathrm{cmc}_{\mathrm{Y}}^{0} + \mathrm{cmc}_{\mathrm{X}}^{0}\,(1-\mathrm{r})$$

Hence the critical micellar concentration of the two surfactants in a given solution, $\mathrm{cmc}_{\mathrm{X}}$ and $\mathrm{cmc}_{\mathrm{Y}}$, depend on parameter r.

$$\mathrm{cmc}_{\mathrm{Y}} = \mathrm{cmc}_{\mathrm{Y}}^{0}\,\mathrm{r}$$

$$\mathrm{cmc}_{\mathrm{X}} = \mathrm{cmc}_{\mathrm{X}}^{0}\,(1-\mathrm{r})$$

Clearly in the absence of surfactant Y, micelles are not formed by surfactant X until the concentration exceeds $\mathrm{cmc}_{\mathrm{X}}^{0}$. If surfactant Y is added to the solution, the $\mathrm{cmc}_{\mathrm{X}}$ changes. In other words the properties of surfactants X and Y in a given solution are linked. We anticipate that for real system cmc(mix) is a function of $\mathrm{c}_{\mathrm{X}}^{0}$ and $\mathrm{c}_{\mathrm{Y}}^{0}$ so that cmc(mix) is a function of ratio r and a quantity θ. The latter takes account of surfactant-surfactant interactions in the micellar pseudophase. Then

$$\mathrm{cmc(mix)} = \mathrm{r}\,\left(\mathrm{cmc}_{\mathrm{Y}}^{0} - \mathrm{cmc}_{\mathrm{X}}^{0}\right)\,\exp[-\theta\,(1-\mathrm{r})] + \mathrm{cmc}_{\mathrm{X}}^{0}$$

For the surfactants X and Y,

$$\mathrm{cmc}_{\mathrm{Y}}(\mathrm{mix}) = \mathrm{r}\,\mathrm{cmc}_{\mathrm{Y}}^{0}\,\exp[-\theta\,(1-\mathrm{r})]$$

and

$$\mathrm{cmc}_{\mathrm{x}}(\mathrm{mix}) = \mathrm{cmc}_{\mathrm{x}}^{0}\,\{1 - \mathrm{r}\,\exp[-\theta\,(1-\mathrm{r})]\}$$

Therefore we envisage that the cmc of solutions containing a mixture of surfactants differs from that for model systems.

We turn attention to the enthalpies of mixed surfactant solutions. In the case of a mixed aqueous solution containing surfactants X and Y, the partial molar enthalpies of the surfactants are anticipated to depend on their concentrations. We characterize a given system by a single enthalpic interaction parameter, h(int).

$$\mathrm{H_x(aq)} = \mathrm{H_x^{\infty}(aq)} + \mathrm{h(int)}\;(\mathrm{c_x/c_r})$$

$$\mathrm{H_Y(aq)} = \mathrm{H_Y^{\infty}(aq)} + \mathrm{h(\ int\ )}\;(\mathrm{c_Y/c_r})$$

Here $\mathrm{H_x^{\infty}(aq)}$ and $\mathrm{H_Y^{\infty}(aq)}$ are the ideal (infinite dilution) partial molar enthalpies of the two monomeric surfactants in aqueous solutions at defined T and p.

The micellar pseudo-separate phase comprises two surfactants amounts $\mathrm{n}_{X}(\ \mathrm{mic}\ )$ and $\mathrm{n}_{Y}(\ \mathrm{mic}\ )$. The mole fractions $\mathrm{x_X(mic)}$ and Extra \left or missing \right are given by equation (k).

$$\mathrm{x_X(mic)} = \mathrm{n_X(mic)}/\left[\mathrm{n_x(mic)} + \mathrm{n_Y(mic)}\right] = 1 - \mathrm{x_Y(mic)}$$

We relate the partial molar enthalpies $H_X(mic)$ and $H_Y(mic)$ in the mixed pseudo-separate phase to the molar enthalpies of surfactants X and Y in pure pseudo-separate micellar phases, $H^*_X(mic)$ and $H^*_Y\ (mic)$ using equations (l) and (m) where U is a surfactant-surfactant interaction parameter.

$$H_X(\ mic\ ) = H^*_X(mic) + [1 - x_X(mic)]^2\ U$$

$$H_Y(mic) = H^*_Y(\ mic\ ) + [x_X(mic)]^2\ U$$

Footnotes

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SECTION OVERVIEW

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1.21.1: Thermodynamics and Mathematics

Thermodynamics provides a basis for the mathematical description of important phenomena such as chemical equilibria, solubilities, densities, and heats of reaction. Chemists have confidence in this approach to chemistry. However for many chemists it is somewhat of a shock to discover that at the heart of mathematics there is serious flaw. In 1931 K. Godel showed that there is a fundamental inconsistency in mathematics [1]. In other words mathematics is incomplete [2]. Nevertheless chemists do not 'throw out the baby with the bathwater'. Atkins [2] notes that it would be foolish to discard mathematics even though there are treacherous regions deep inside its structure.

Footnotes

[1] An interesting account is given by D. R. Hofstadter in Godel, Esher and Bach;An Extended Golden Braid, Vintage, New York, 1980.

[2] P. W. Atkins, Galileo's Finger, Oxford, 2003, chapter 10.

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1.21.2: Thermodynamic Energy

The thermodynamic energy U of a closed system increases when work w is done by the surroundings on the system and heat q flows from the surroundings into the system.

$$\Delta \mathrm{U} = \mathrm{q} + \mathrm{w}$$

Equation (a) uses the acquisitive convention. In effect we record all changes from the point of view of the system.

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1.21.3: Thermodynamic Energy: Potential Function

The Master Equation states that the change in thermodynamic energy of a closed system is given by equation (a).

$$\mathrm{dU} = \mathrm{T\,dS} - \mathrm{p\,dV} - \mathrm{A\,d\xi}; \quad \mathrm{A\,d\xi} \geq 0$$

At constant entropy (i.e. $\mathrm{dS} = 0$) and constant volume (i.e. $\mathrm{dV} = 0$), equation (a) leads to equation (b).

$$\mathrm{dU} = -\mathrm{A\,d\xi}$$

But

$$A\,d\xi \geq 0$$

Therefore all spontaneous processes at constant S and constant V take place in a direction for which the thermodynamic energy decreases.

The latter statement shows the power of thermodynamics in that it is quite general; we have not stated the nature of the spontaneous process. Of course chemists are interested in those cases where the spontaneous process is chemical reaction. Thus we have a signal of what happens to the energy of the system; the key word here is spontaneous.

In the context of most chemists interests, equation (b) is not terribly helpful. Chemists do not normally run their experiments at constant S and constant V. In fact it is not obvious how one might do this. Nevertheless equation (b) is important finding its application when we turn to other thermodynamic variables which can be used as thermodynamic potentials; e.g. Gibbs energy.

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1.21.4: Thermodynamic Potentials

The following important equations describe changes in thermodynamic energy, enthalpy, Helmholtz energy and Gibbs energy of a closed system.

$$p\mathrm{dU} = \mathrm{T\,dS} - \mathrm{p\,dV} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mu_{\mathrm{j}}\,\mathrm{dnj_j}$$

$$\mathrm{dH} = \mathrm{T\,dS} + \mathrm{V\,dp} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mu_{\mathrm{j}}\,\mathrm{dnj_j}$$

$$\mathrm{dF} = -\mathrm{S\,dT} - \mathrm{p\,dV} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mu_{\mathrm{j}}\,\mathrm{dnj_j}$$

$$\mathrm{dG} = -\mathrm{S\,dT} + \mathrm{V\,dp} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mu_{\mathrm{j}}\,\mathrm{dnj_j}$$

These four differential equations relate, for example, the change in $\mathrm{U},\ \mathrm{H},\ \mathrm{F}$ and G with the change in amount of each chemical substance, $\mathrm{d}n_j$. These four equations are integrated [1] to yield the following four equations.

$$\mathrm{U} = \mathrm{T\,S} - \mathrm{p\,V} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mathrm{n_j}\,\mu_{\mathrm{j}}$$

$$\mathrm{H} = \mathrm{T\,S} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mathrm{n_j}\,\mu_{\mathrm{j}}$$

$$\mathrm{F} = -\mathrm{p\,V} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mathrm{n_j}\,\mu_{\mathrm{j}}$$

$$G = \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mathrm{n_j}\,\mu_{\mathrm{j}}$$

The latter equation is particularly useful because it signals that the total Gibbs energy of a system is given by the sum of the products of amounts and chemical potentials of all substances in the system. In the case of an aqueous solution containing $\mathrm{n_1}$ moles of water and n_j moles of chemical substance j, the Gibbs energy of the solution is given by equation (i).

$$\mathrm{G(aq)} = \mathrm{n_1}\,\mu_1\mathrm{(aq)} + \mathrm{n_j}\,\mu_{\mathrm{j}}\mathrm{(aq)}$$

In conjunction with equation (i) we do not have to attach the phrase ‘at temperature T and pressure p’. Similarly the volume of the solution is given by equation (j) where $\mathrm{V}_1\mathrm{(aq)}$ and $\mathrm{V}_j\mathrm{(aq)}$ are the partial molar volumes of solvent and solute respectively.

$$\mathrm{V(aq)} = \mathrm{n_1\,V_1(aq)} + \mathrm{n_j\,V_j(aq)}$$

The same argument applies in the case of a solution prepared using $\mathrm{n_1}$ moles of solvent water, $\mathrm{n_x}$ moles of solute X and $\mathrm{n_y}$ moles of solute Y. Then, for example,

$$\mathrm{G(aq)} = \mathrm{n_1}\,\mu_1\mathrm{(aq)} + \mathrm{n_x}\,\mu_{\mathrm{x}}\mathrm{(aq)} + \mathrm{n_y}\,\mu_{\mathrm{y}}\mathrm{(aq)}$$

The analogue of equation (j) also follows but **only** if $\mathrm{n_x}$ and $\mathrm{n_y}$ are independent of pressure. If these two solutes are in chemical equilibrium [eg. $\mathrm{X(aq)} \Leftrightarrow \mathrm{Y(aq)}$, amounts $\mathrm{n_x^{eq}}$ and $\mathrm{n_y^{eq}}$ respectively], then account must be taken of the dependences of $\mathrm{n_x^{eq}}$ and $\mathrm{n_y^{eq}}$ on pressure at fixed temperature and (with reference to entropies and enthalpies) on temperature at fixed pressure.

The simple form of equations (i) and (k) emerge from equation (h) because other than the composition variables, the other differential terms dT and dp in equation (d) refer to change in intensive variables. For this reason chemists find it advantageous to describe chemical properties in the $\mathrm{T-p}$-composition domain.

The relationships between thermodynamic potentials are described as Legendre transforms [2]. The product term $\mathrm{T\,S}$ may be called bounded energy. Then the Helmholtz energy ($\mathrm{F = U - T\,S}$) is the free internal energy and the Gibbs energy ($\mathrm{G = H - T\,S}$) is the free enthalpy. These comments help to understand the old designations of free Helmholtz energy (together with symbol F), free Gibbs energy and the still currently used (in the French scientific literature) free enthalpy.

Footnotes

[1] The term "integrated" in this context deserves comment. Within the set of variables, $\mathrm{p - V - T - S}$, p and T are intensive whereas V and S are extensive variables. Similarly μ_j is intensive whereas $\mathrm{n_j}$ is extensive. These are the conditions for operating Euler's integration method. Still the word "integrate" in the present context has been used in subtle arguments when Euler's theorem is not invoked.

E. F. Caldin [Chemical Thermodynamics, Oxford, 1958, p. 166] identifies $\mathrm{T,\ p\ and}\ \mu_j$ as intensive and then integrates by gradual increments of the amount of each chemical substance, keeping the relative amounts constant.

K. Denbigh [The Principles of Chemical Equilibrium, Cambridge, 1971, 3rd edn. p. 93] uses a similar argument, but comments that development of the equations (e) to (h) is not mathematical in the sense that the variables are simple. Rather we use our physical knowledge in that intensive variables do not depend on the state of the system.

E. A. Guggenheim [Thermodynamics, North-Holland, Amsterdam, 1950, 2nd edn. p. 23] states that the equations (a) to (d) can be integrated by following the artifice when \(\mathrm{dT} = 0, \mathrm{~dp = 0}\) and each $\mathrm{n_j}$ is changed by the same proportions as are the extensive variables S and V.

{The term artifice is used here to mean a 'device', skill rather than "trickery" or "something intended to deceive"; Pocket Oxford Dictionary, Oxford 1942, 4th edn. and Cambridge International Dictionary of English, Cambridge, 1995.

[2] There is a pleasing internal consistency between the definitions advanced at this stage

a.
$$\mathrm{U = T\,S - p\,V + \sum_{j=1}^{j=k} n_j\,\mu_j}$$

Then (cf. definition of G)

$$\mathrm{G = U - T\,S + p\,V}$$

b.
$$F = -p\,V + \sum_{j=1}^{j=k} n_j\,\mu_j$$

Then from (a),

c.
$$\mathrm{H = T\,S + \sum_{j=1}^{j=k} n_j\,\mu_j}$$

Then from (a),

d. Combining equations. relating G and U to H yields $\mathrm{G = H - T\,S}$. Similarly the connections of G and F to U give $\mathrm{G = F + p\ V}$

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1.21.5: Thermodynamic Stability: Chemical Equilibria

At fixed temperature and pressure, all spontaneous processes lower the Gibbs energy of a closed system. Thermodynamic equilibrium corresponds to the state where G is a minimum and the affinity for spontaneous change is zero. The equilibrium is stable. The condition for chemical thermodynamic stability is that

$$(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}} < 0$$

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1.21.6: Thermodynamic Stability: Thermal, Diffusional and Hydrostatic

On the bench in front of a chemist is a stoppered flask containing a liquid mixture, ethanol + water, at temperature T and ambient pressure p. The chemist might wonder why the homogeneous liquid does not spontaneously separate into two liquids, say water-rich and alcohol-rich mixtures. The chemist might also wonder why the mixture does not spontaneously produce a system which comprises a warm liquid mixture and a cold liquid mixture. Yet the fact that these changes do not occur spontaneously leads to the conclusion that the conditions in operation which forbid these changes can be traced to the Second Law of Thermodynamics, prompted by the word 'spontaneously' used above [1].

Thermal Stability

Initially a given closed system has thermodynamic energy $2\mathrm{U}$ and volume $2\mathrm{V}$. We imagine that the mixture does in fact separate into two liquids, both at equilibrium, having energy $\mathrm{U}+\delta\mathrm{U}$ with volume V, and energy $\mathrm{U}-\delta\mathrm{U}$ also with volume V. The overall change in entropy at constant overall composition is given by equation (a).

$$\delta \mathrm{S}=\mathrm{S}(\mathrm{U}+\delta \mathrm{U}, \mathrm{V})+\mathrm{S}(\mathrm{U}-\delta \mathrm{U}, \mathrm{V})-\mathrm{S}(2 \mathrm{U}, 2\ \mathrm{V})$$

The change in entropy can be understood in terms of a Taylor expansion for a change at constant volume V. Thus

$$\delta S=\left(\frac{\partial^2 S}{\partial U^2}\right)_{V, \xi}(\delta U)^2$$

However at constant V and composition ξ, the Second Law of Thermodynamics requires that $\delta \mathrm{S}$ is positive for all spontaneous processes. The fact that such a change is not observed requires that $\left(\frac{\partial^2 \mathrm{S}}{\partial \mathrm{U}^2}\right)$ is negative. But

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{U}}\right)_{\mathrm{V}, \xi}=\mathrm{T}^{-1}$$

Then

$$\left(\frac{\partial^2\ \mathrm{S}}{\partial \mathrm{U}^2}\right)_{\mathrm{V}, \xi}=\frac{\partial}{\partial \mathrm{U}}\left(\mathrm{T}^{-1}\right)=-\frac{1}{\mathrm{T}^2}\left(\frac{\partial \mathrm{T}}{\partial \mathrm{U}}\right)_{\mathrm{V}, \xi}=-\frac{1}{\mathrm{T}^2\, \mathrm{C}_{\mathrm{V} \xi}}$$

In order for the latter condition to hold, $\mathrm{C}_{\mathrm{V}\xi}$ must be positive. This is therefore the condition for thermal stability. In other words we will not observe spontaneous separation into hot and cold domains in that heat capacities are positive variables.

Diffusional Stability

A given system at temperature T and pressure p contains $2\,\mathrm{n_i}$ moles of each i-chemical substance, for $\mathrm{i}=1,2,3 \ldots$. The system is divided into two parts such that each part at temperature T and pressure p contains $\mathrm{n_i}$ moles of each chemical substance for $\mathrm{i}=2,3,4, \ldots$. However one part contains $\mathrm{n}_1+\Delta \mathrm{n}_1$ moles and the other part contains $\mathrm{n}_1-\Delta \mathrm{n}_1$ moles of chemical substance 1. Then the change in Gibbs energy $\delta \mathrm{G}$ is given by equation (e).

$$\begin{array}{c}\delta \mathrm{G}=\mathrm{G}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1+\Delta \mathrm{n}_1, \mathrm{n}_2, \mathrm{n}_3 ..\right]+\mathrm{G}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1-\Delta \mathrm{n}_1, \mathrm{n}_2, \mathrm{n}_3 ..\right] \\ -\mathrm{G}\left[\mathrm{T}, \mathrm{p}, 2\,\mathrm{n}_1, 2\,\mathrm{n}_2, 2\,\mathrm{n}_3 ..\right]\end{array}$$

In terms of a Taylor expansions,

$$\delta G=\left(\frac{\partial^2 G}{\partial n_1^2}\right)_{T, p, n(2), n(3) ..}\left(\delta n_1\right)^2$$

But chemical potential,

$$\mu_1=\left(\frac{\partial \mathrm{G}}{\partial \mathrm{n}_1}\right)_{\mathrm{T}, \mathrm{p}, \mathrm{n}(2), \mathrm{n}(3) \ldots}$$

Then

$$\left(\frac{\partial^2 \mathrm{G}}{\partial \mathrm{n}_1^2}\right)_{\mathrm{T}, \mathrm{p}, \mathrm{n}(2), \mathrm{n}(3) \ldots}=\left(\frac{\partial \mu_1}{\partial \mathrm{n}_1}\right)_{\mathrm{T}, \mathrm{p}, \mathrm{n}(2), \mathrm{n}(3) \ldots .}$$

We conclude that spontaneous separation of the system into parts rich and depleted in chemical substance-1 would occur if $\left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,p,n(2),n(3)}$ is negative. But this process is never observed. Hence the condition for diffusional (or material) stability is that $\left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,p,n(2),n(3)....} > 0$. Further if we add $\delta \mathrm{n}_1$ moles of chemical substance to a closed system at fixed $\mathrm{T}, \mathrm{p}, \mathrm{n}_2, \mathrm{n}_3 ...$, chemical potential μ1 must increase.

Hydrostatic Stability

A given system at temperature T and chemical composition ξ has volume 2V. We imagine that a infinitely thin partition exists separating the system into two parts having equal volumes V. The Helmholtz energy of the system volume 2V is given by equation (i).

$$\mathrm{F} = \mathrm{F}[\mathrm{T}, 2\ \mathrm{V}, \xi]$$

The Helmholtz energy of the two parts, volume V is given by equation (j).

$$\mathrm{F} = \mathrm{F}[\mathrm{T}, \mathrm{V}, \xi]$$

The partition is envisaged as moving to produce two parts having volumes $(\mathrm{V} + \delta \mathrm{V})$ and $(\mathrm{V} - \delta \mathrm{V})$. Then at constant composition the change in Helmholtz energy is given by equation (k).

$$\delta \mathrm{F} = \mathrm{F}[\mathrm{T}, \mathrm{V} + \delta \mathrm{V}] + \mathrm{F}[\mathrm{T}, \mathrm{V} - \delta \mathrm{V}] - \mathrm{F}[\mathrm{T}, 2\ \mathrm{V}]$$

Then using Taylor's theorem,

$$\delta \mathrm{F} = \left(\partial^2\ \mathrm{F}/\partial \mathrm{V}^2\right)_{\mathrm{T}}\ (\partial \mathrm{V})^2$$

Hence [2]

$$\left(\partial^2\ \mathrm{F}/\partial \mathrm{V}^2\right)_{\mathrm{T}} = -(\partial \mathrm{p}/\partial \mathrm{V})_{\mathrm{T},\xi}$$

Irrespective of the sign of $(\delta \mathrm{V})$, we conclude that $\delta \mathrm{F}$ would be negative in the event that $(\partial \mathrm{p}/\partial \mathrm{V})_{\mathrm{T},\xi}$ is positive. But we never witness such a spontaneous separation of a system into two parts. In other words $(\partial \mathrm{p}/\partial \mathrm{V})_{\mathrm{T},\xi} < 0$. Hence,

$$\kappa_{\mathrm{T}} = -\left(\frac{1}{\mathrm{V}}\right)\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} > 0$$

Therefore for a system at fixed composition and temperature, if we as observers of this system increase the pressure p, the volume of the system decreases. This is the condition of hydrostatic (or, mechanical) stability [1].

Physical Consequences of Stability

Taken together, conditions for thermal stability $(\mathrm{C}_{\mathrm{V}\xi} > 0)$ and for mechanical stability $(\kappa_{\mathrm{T}} > 0)$ have further consequences [3]. Since,

$$\sigma = \mathrm{C}_{\mathrm{V}\xi}/\mathrm{V} + \frac{\mathrm{T}\ (\alpha_{\mathrm{p}})^2}{\kappa_{\mathrm{T}}}$$

Then isobaric heat capacities and heat capacitances , $\sigma\ (= \mathrm{C}_{\mathrm{pg}}/\mathrm{V})$ are positive for stable phases.

Furthermore, heat capacities and compressibilities are related by equation (p).

$$\frac{\mathrm{K}_{\mathrm{S}}}{\mathrm{K}_{\mathrm{T}}} = \frac{\mathrm{C}_{\mathrm{V}}}{\mathrm{C}_{\mathrm{p}}}$$

Hence the isentropic compressibility κ_{S} of a stable phase must also be positive. In summary,

$$\mathrm{C}_{\mathrm{pm}} \geq \mathrm{C}_{\mathrm{Vm}_{\mathrm{m}}} > 0$$

$$\kappa_{\mathrm{T}} \geq \kappa_{\mathrm{S}} > 0$$

Footnotes

[1] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979, chapter 7.

[2] By definition, $\mathrm{F} = \mathrm{F}[\mathrm{T}, \mathrm{V}, \xi]$. The total differential of the latter equation is as follows.

$$\mathrm{dF} = \left(\frac{\partial \mathrm{F}}{\partial \mathrm{T}}\right)_{\mathrm{V},\xi} \mathrm{dT} + \left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}}\right)_{\mathrm{T},\xi} \mathrm{dV} + \left(\frac{\partial \mathrm{F}}{\partial \xi}\right)_{\mathrm{T,V}} \mathrm{d}\xi$$

But (the 'all-minus' equation)

$$\mathrm{dF} = -\mathrm{S}\,\mathrm{dT} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi$$

Then,

$$\left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}}\right)_{\mathrm{T},\xi} = -\mathrm{p}$$

Or,

$$\left(\frac{\partial^2 \mathrm{F}}{\partial \mathrm{V}^2}\right)_{\mathrm{T},\xi} = -\left(\frac{\partial \mathrm{p}}{\partial \mathrm{V}}\right)_{\mathrm{T},\xi}$$

[3] H. B. Callen, Thermodynamics and an Introduction to Thermostatistics, Wiley, New York, 2nd edn., 1985, pp.209-210.

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1.21.7: Thermodynamics and Kinetics

A given system at temperature T and pressure p is prepared using $\mathrm{n_1}$ moles of water(ℓ), the solvent, together with $\mathrm{n_X^0}$ and $\mathrm{n_Y^0}$ moles of chemical substances X and Y respectively at time '$\mathrm{t = 0}$'. The molalities of these solutes are $\mathrm{m_X^0 \, (= n_X^0/n_1 \, M_1 = n_X^0/w_1)}$ and $\mathrm{m_Y^0 \, (= n_Y^0/n_1 \, M_1 = n_Y^0/w_1)}$ respectively at time '$\mathrm{t = 0}$'; the concentrations are $\mathrm{c_X^0 \, (= n_{XA}^0/V)}$ and $\mathrm{c_Y^0 \, (= n_Y^0/V)}$ respectively.

Spontaneous chemical reaction leads to the formation of product Z. Here we consider this spontaneous change from the standpoints of chemical thermodynamics and chemical kinetics.

Thermodynamics

The spontaneous chemical reaction is driven by the affinity for chemical reaction, A [1]. At each stage of the reaction the composition is described by the extent of reaction ξ. The affinity A is defined by the thermodynamic independent variables, $\mathrm{T, \ p \ and \ \xi}$. Thus

$$\mathrm{A = A[T, p, \xi]}$$

Therefore

$$\mathrm{dA = \left(\frac{\partial A}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial A}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial A}{\partial \xi}\right)_{T,p} d\xi}$$

At constant T and p,

$$\mathrm{dA = \left(\frac{\partial A}{\partial \xi}\right)_{T,p} d\xi}$$

In terms of thermodynamics, the reference point is thermodynamic equilibrium where the affinity for spontaneous change is zero and the composition is ξ^{eq}.

Chemical Kinetics

In the context of chemical reaction in solution, the system under study is, conventionally, a very dilute solution so that from a macroscopic standpoint the system at '$\mathrm{t = 0}$' is slightly displaced from equilibrium where A is zero. Thus chemists exploit their skill in monitoring for a solution the change with time of the absorbance at fixed wavelength, electrical conductivity, pH…. In a key assumption, the rate of change of composition $\mathrm{d\xi/ \, dt}$ is proportional to the affinity A for spontaneous change[2];

$$\mathrm{d\xi/dt = L \, A}$$

Here L is a phenomenological constant describing, in the present context, the phenomenon of spontaneous chemical reaction.

In general terms for processes at fixed temperature and pressure, the phenomenological property L is related the isobaric – isothermal dependence of affinity A on extent of chemical reaction by a relaxation time $\tau_{\mathrm{T,p}}$. Thus

$$\mathrm{L^{-1} = -\left(\frac{\partial A}{\partial \xi}\right)_{T,p} \tau_{T,p}}$$

Relaxation time \(\tau_{\mathrm{T},\mathrm{p}\) is a macroscopic property of a given system (at defined T and p) which chemists understand in terms of spontaneous chemical reaction (in a closed system). The task for chemists is to identify the actual chemical reaction in a given closed system.

Thermodynamics and Chemical Kinetics

In most treatments of chemical reactions the reference state is chemical equilibrium [3] where away from equilibrium the property dA equals the affinity A on the grounds that at equilibrium, A is zero; $\mathrm{A = A - A^{eq} = A - 0}$. Hence combination of equations (c), (d) and (e) yields the key kinetic-thermodynamic equation.

$$\mathrm{\frac{d\xi}{dt} = -A \, (\tau_{T,p})^{-1} \left(\frac{\partial A}{\partial \xi}\right)_{T,p}^{-1}}$$

Equation (6) relates the rate of change of composition to the affinity for chemical reaction and relaxation time $\tau_{\mathrm{T,p}}$. Equation (f) is therefore the key equation describing spontaneous chemical reaction in a closed system. In this context we stress the importance of equation (f).

Law of Mass Action

Equation (f) is an interesting and important description of the kinetics of chemical reaction. In fact the link between the rate of chemical reaction ($\mathrm{d}\xi/\mathrm{dt}$) and the affinity for spontaneous change A is intuitively attractive. However while one may monitor the dependence of composition on time, $\mathrm{d}\xi/\mathrm{dt}$, it is not immediately obvious how one might estimate the affinity A and the property $\left(\frac{\partial \mathrm{A}}{\partial \xi}\right)_{\mathrm{T,p}}$ at time t. The Law of Mass Action offers a way forward although this law does not emerge from either the First or Second Laws of Thermodynamics. As Hammett [4] notes the Law of Mass Action was 'first derived from limited observations' and became 'established through accumulation of observations with the principle and in the absence of contradictory evidence'. After the 'Dark Ages', came the renaissance and 'Bartlett and Ingold and Peterson… accepting without question or comment the validity of the law of mass action' [4].

The link back to thermodynamics was constructed using Transition State Theory developed by Eyring and described by Glasstone, Laidler and Eyring [5]. Therefore the phenomenological Law of Mass Action was brought into the fold of thermodynamics by offering a language which allowed activation parameters to be understood in terms of, for example, standard enthalpies and standard isobaric heat capacities of activation.

Footnotes

[1] I. Prigogine and R. Defay, Chemical Thermodynamics, (transl. D. H. Everett) Longmans Green, London, 1954.

[2] See for example, M. J. Blandamer, Introduction to Chemical Ultrasonics, Academic Press, London, 1973.

[3] E. F. Caldin, Fast Reactions in Solution, Blackwell, Oxford, 1964.

[4] L. P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, McGraw-Hill, New York, 2nd. edition, 1970, p.94.

[5] S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York,1941.

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1.21.8: Third Law of Thermodynamics

The Third Law of Thermodynamics states that the entropy and the heat capacity of a perfect crystal vanish in the limit of zero kelvin [1].

When a system is heated, energy is stored in the form of molecular vibrations leading to an increase in entropy. The isochoric heat capacity is related to the differential dependence of energy on temperature at equilibrium.

A more detailed analysis is required if phase changes and inter-component mixing is involved. Here there are additional contributions to the change in entropy accompanying irreversible processes which Gurney describes as the cratic part of the entropy [2]. In a certain sense an isentropic process is ‘a draw between Maxwell’s demon and a natural process’ [3].

Footnotes.

[1] K. S. Pitzer, Thermodynamics, McGraw-Hill, New York, 3rd. edn.,1965.

[2] R. W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.

[3] A. B. Pippard, The Elements of Classical Thermodynamics, University Press, Cambridge ,1957, p.99.

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SECTION OVERVIEW

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1.22.1: Volume: Partial Molar: General Analysis

At temperature T, pressure p and equilibrium, the volume of a closed system containing i-chemical substances where the amounts can be independently varied, is defined by the following equation.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2, \ldots \ldots \mathrm{n}_\mathrm{i}\right]$$

Or, in general terms according to Euler's theorem,

$$\mathrm{V} = \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{n}_\mathrm{j}\, \mathrm{V}_\mathrm{j}$$

where

$$\mathrm{V}_\mathrm{j} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_\mathrm{j}}\right)_{\mathrm{T,p,n_{i\neq j}}}$$

The general differential of equation (b) has the following form.

$$\mathrm{dV} = \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{n}_\mathrm{j}\, \mathrm{dVV}_\mathrm{j} + \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{V}_\mathrm{j}\, \mathrm{dnn}_\mathrm{j}$$

The general differential of equation (a) has the following form

$$\mathrm{dV} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p,n_i}} \mathrm{dT} + \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,n_i}} \mathrm{dp} + \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_\mathrm{j}}\right)_{\mathrm{T,p,n_{i\neq j}}} \mathrm{dn}_\mathrm{j}$$

Comparison of equations (d) and (e) shows that

$$0 = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p,n_i}} \mathrm{dT} - \left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,n_i}} \mathrm{dp} + \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{n}_\mathrm{j}\, \mathrm{dVj}_\mathrm{j}$$

Equation (f) is the Gibbs-Duhem Equation with respect to the volumetric properties of a closed system at equilibrium.

Application

A given closed system contains n_1 moles of solvent (water) and n_j moles of solute j at temperature T and pressure p. The system is at equilibrium where G is a minimum, the affinity for spontaneous change A is zero and the composition-organisation ξ^{eq}. The dependent variable volume V is defined using a set of independent variables; equation (g).

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}\right]$$

Equation (k) has an interesting property. If we multiply the extensive variables n_1 and n_j by a factor k, the volume of the system equals $(\mathrm{V.\ k})$. In terms of Euler's Theorem [1], the variable V linked to the variables n_1 and n_j is a homogeneous function of the first degree. The important consequence is the following key relation.

$$\mathrm{V} = \mathrm{n}_1\, \mathrm{V}_1 + \mathrm{n}_\mathrm{j}\, \mathrm{V}_\mathrm{j}$$

where

$$\mathrm{V}_1 = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_1}\right)_{\mathrm{T,p,n(j)}}$$

and

$$\mathrm{V}_\mathrm{j} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_\mathrm{j}}\right)_{\mathrm{T,p,n(1)}}$$

We do not have to specify the conditions 'at constant T and p' in conjunction with equation (h) which is a mathematical identity.

Footnote

[1] Degree of Homogeneity

At temperature T and pressure p, the volume of a closed system containing n_j moles of each chemical substance j is given by

$$\mathrm{V} = \mathrm{V}\left[\mathrm{n}_1, \mathrm{n}_2 \ldots \ldots \ldots \ldots \ldots \mathrm{n}_\mathrm{k}\right]$$

The property volume has unit degree of homogeneity. That is to say – if the amount of each substance is increased by a factor λ then the volume increases by the same factor. Thus

$$\mathrm{V}\left[\lambda\mathrm{n}_1, \lambda\mathrm{n}_2 \ldots \ldots \ldots \ldots \ldots \lambda\mathrm{n}_\mathrm{k}\right] = \lambda\,\mathrm{V}\left[\mathrm{n}_1, \mathrm{n}_2 \ldots \ldots \ldots \ldots \ldots \mathrm{n}_\mathrm{k}\right]$$

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1.22.10: Volume: Aqueous Binary Liquid Mixtures

For binary aqueous mixtures (at ambient pressure and fixed temperature) there are two interesting reference points.

i. The molar volume of the pure liquid component 2, $V_2^*(\lambda)$.
ii.

In the latter case we imagine that each molecule of liquid 2 is surrounded by an infinite expanse of water. With gradual increase in x_2, so (on average) the molecules of liquid 2 move closer together.

Typically Aqueous Mixtures

For these systems $[V_2^\infty(\text{mix}) - V_2^*(\lambda)]$ is negative. But this pattern is not unique to aqueous systems. The unique feature is the decrease in $[V_2(\text{mix}) - V_2^*(\lambda)]$ with increase in x_2 at low x_2 [1]. In fact with increase in hydrophobicity of chemical substance 2, the decrease is more striking and the minimum in $[V_2(\text{mix}) - V_2^*(\lambda)]$ occurs at lower x_2. At mole fractions beyond x_2 $[V_2(\text{mix}) - V_2^*(\lambda)]$ increases with increase in x_2. Many explanations have been offered for this complicated pattern. The following is one explanation.

The negative $[V_2^\infty(\text{mix}) - V_2^*(\lambda)]$ is accounted for in terms of a liquid clathrate in which part of the hydrophobic group 'occupies' a guest site in the liquid water 'lattice'. The decrease in $[V_2(\text{mix}) - V_2^*(\lambda)]$ is accounted for in terms of an increasing tendency towards a liquid clathrate hydrate structure. With increase in x_2 there comes a point where there is insufficient water to construct the liquid clathrate host. Hence $[V_2(\text{mix}) - V_2^*(\lambda)]$ increases [2,3].

Typically Non-Aqueous Systems

Although $[V_2^\infty(\text{mix}) - V_2^*(\lambda)]$ is negative no minimum is observed in $[V_2(\text{mix}) - V_2^*(\lambda)]$.

Footnotes

[1] See for example; fluoroalcohols(aq); C. H. Rochester and J. R. Symonds, J. Fluorine Chem.,1974,**4**,141.

[2] F. Franks, Ann. N. Y. Acad. Sci.,1955,**125**,277.

[3] For many binary aqueous mixtures the patterns in volume related properties often identify transition points at 'structurally interesting compositions'; G. Roux, D. Roberts, G. Perron and J. E. Desnoyers, J. Solution Chem.,1980,**9**,629.

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1.22.11: Volumes: Liquid Mixtures: Binary: Method of Tangents

The 'Method of Tangents' is an important technique which is readily illustrated using the volumetric properties of binary liquid mixtures. The starting point is (as always?) the Gibbs - Duhem Equation which leads to equation (a) for systems at fixed temperature and pressure.

$$n_1\, dV_1(mix) + n_2\, ddV_2(mix) = 0$$

Dividing by $(n_1 + n_2)$,

$$x_1\, d\, V_1(mix) + x_2\, dV_2(mix) = 0$$

The molar volume is given by equation (c).

$$V_m(mix) = x_1\, V_1(mix) + x_2\, V_2(mix)$$

Hence (at equilibrium, fixed temperature and pressure) the differential dependence of $V_m(mix)$ on mole fraction x_1 is given by equation (d).

$$\frac{dV_m(mix)}{dx_1} = V_1(mix) + x_1 \left[\frac{dV_1(mix)}{dx_1}\right] + V_2(mix) \left[\frac{dx_2}{dx}\right] + x_2 \left[\frac{dV_2(mix)}{dx_1}\right]$$

From the Gibbs-Duhem equation,

$$x_1 \frac{dV_1(mix)}{dx_1} + x_2 \frac{dV_2(mix)}{dx_1} = 0$$

[Note the common denominator.] Also $x_1 + x_2 = 1$. And so,

$$dx_1 = -dx_2$$

Therefore,

$$\frac{dVm_m(mix)}{dx_1} = V_1(mix) - V_2(mix)$$

Combination of equations (c) and (g) yields the following equation.

$$V_m(mix) = x_1\, V_1(mix) + x_2 \left[V_1(mix) - \frac{dV_m(mix)}{dx_1}\right]$$

Further,

$$x_1\, V_1(mix) + x_2\, V_1(mix) = V_1(mix)$$

Hence,

$$V_1(mix) = V_m(mix) + (1 - x_1) \frac{dV_m(mix)}{dx_1}$$

At a given mole fraction, we determine the molar volume of the mixture $V_m(mix)$ and its dependence on mole fraction. $[dVm_m(mix)/dx_1]$ is the gradient of the **tangent** at mole fraction x_1 to the curve recording the dependence of $V_m(mix)$ on x_1; hence the name of this method of data analysis. This analysis is relevant because, as commented above, we can determine the variables $V_1^*(\ell), V_2^*(\ell)$ and $V_m(mix)$.

Another approach is based on excess molar volumes V_m^E and their dependence on mole fraction at fixed temperature and pressure. Since

$$V_m(id) = x_1\, V_1^*(\ell) + x_2\, V_2^*(\ell)$$

And

$$V_m^E = V_m(mix) - V_m(id)$$

From equations (c), and (k),

$$V_m^E = x_1\,[V_1(mix) - V_1^*(\ell)] - x_2\,[V_2(mix) - V_2^*(\ell)]$$

We define excess partial molar volumes;

$$V_1^E(mix) = V_1(mix) - V_1^*(\ell)$$

and

$$V_2^E(mix) = V_2(mix) - V_2^*(\ell)$$

Hence the excess molar volume of the mixture is related to two excess partial molar volumes.

$$V_m^E = x_1\,V_1^E(mix) + x_2\,V_2^E(mix)$$

We use equation (m) to obtain the differential dependence of V_m^E on mole fraction x_1.

$$\begin{aligned} dV_m^E =& [V_1(mix) - V_1^*(\ell)] + x_1\left[\frac{dV_1(mix)}{dxx_1}\right] \\ &+ \left[\frac{dx_2}{dxx_1}\right][V_2(mix) - V_2^*(\ell)] + x_2\left[\frac{dV_2(mix)}{dx_1}\right] \end{aligned}$$

We write the Gibbs - Duhem equation in the form shown in equation (e) together with equation (p). Hence,

$$dV_m^E/dx_1 = V_1^E - V_2^E$$

or,

$$V_2^E = V_1^E - dV_m^E/dx_1$$

Hence using equation (o),

$$V_m^E = x_1\,V_1^E + x_2\,V_1^E - x_2\,dVV_m^E/dx_1$$

Thus,

$$V_1^E = V_m^E + (1 - x_1)\;d\;V_m^E/dx_1$$

Equation (t) is the excess form of equation (j). A plot of V_m^E against x_1 shows a curve passing through '$V_m^E = 0$' at $x_1 = 0$ and $x_1 = 1$. Other than these two reference points, thermodynamics does not define the shape of the plot of V_m^E against x_1. Thermodynamics does not define the shape of the plot of V_1^E against x_1 other than to require that at $x_1 = 1$, V_1^E is zero. An interesting feature is the sign and magnitude of V_1^E in the limit that $x_1 = 0$; i.e. at $x_2 = 1$.

The volumetric properties of a binary liquid (homogeneous) mixture is summarized by a plot of excess molar volume V_m^E against, for example, mole fraction x_1. In fact this type of plot is used for many excess molar properties including G_m^E and H_m^E. Here we consider a general excess molar property X_m^E. The corresponding excess partial molar property of chemical substance 1 is X_1^E which is related to X_m^E and the dependence of X_m^E on x_1 at mole fraction x_1,

$$X_1^E = X_m^E + (1 - x_1)\;dXX_m^E/dx_1$$

Calculation of X_1^E requires the gradient dXm/dx_1 as a function of mole fraction composition. The way forward involves fitting the dependence of X_m^E on x_1 to a general equation and then calculating dXm/dx_1 using the derived parameters [1-4].

Footnotes

[1] C. W. Bale and A. D. Pelton, Metallurg. Trans.,1974,**5**,2323.

[2] C. Jambon and R. Philippe, J.Chem.Thermodyn.,1975,**7**,479.

[3] M. J. Blandamer, N. J. Blundell, J. Burgess, H. J. Cowles and I. M. Horn, J. Chem. Soc. Faraday Trans.,1990,**86**,277.

[4] A description of a useful procedure for non-linear least squares analysis is given by W. E. Wentworth, J.Chem.Educ.,1965,**42**,96.

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1.22.12: Volume of Reaction: Dependence on Pressure

Consider a chemical equilibrium between two solute $\mathrm{X(aq)}$ and $\mathrm{Y(aq)}$ in aqueous solution at fixed T and p. We assume that the thermodynamic properties of the two solutes are ideal. The chemical equilibrium is be expressed as follows.

$$\mathrm{X(aq) \Leftrightarrow Y(aq)}$$

The (dimensionless intensive) degree of reaction α is related to the equilibrium constant $\mathrm{K^0}$ using equation (b) [1].

$$\alpha = \mathrm{K^0}/\left(1+\mathrm{K^0}\right)$$

At fixed temperature,

$$\frac{\mathrm{d}\alpha}{\mathrm{dp}} = \frac{\mathrm{K^0}}{\left(1+\mathrm{K^0}\right)^2}\,\frac{\mathrm{d\ln\left(K^0\right)}}{\mathrm{dp}}$$

Or,

$$\frac{\mathrm{d}\alpha}{\mathrm{dp}} = -\frac{\mathrm{K^0}}{\left(1+\mathrm{K^0}\right)^2}\,\frac{\Delta_\mathrm{r}\mathrm{V^0(aq)}}{\mathrm{R\,T}}$$

$\Delta_\mathrm{r}\mathrm{V^0(aq)}$ is the limiting volume of reaction. The (equilibrium) volume of the system at a defined T and p is given by equation (e).

$$\mathrm{V(aq) = n_x\,V_x^\infty(aq) + n_Y\,V_Y^\infty(aq) + n_1\,V_1^*(\ell)}$$

$\mathrm{V_1^*(\ell)}$ is the molar volume of solvent, water. If $\mathrm{n_x^0}$ is total amount of solute, (i.e. X and Y) in the system,

$$\mathrm{V(aq) = (1-\alpha)\,n_X^0\,V_x^\infty(aq) + \alpha\,n_X^0\,V_Y^\infty(aq) + n_1\,V_1^*(\ell)}$$

Or,

$$\mathrm{V(aq) = n_X^0\,V_x^\infty(aq) + \alpha\,n_X^0\,\Delta_r V^\infty(aq) + n_1\,V_1^*(\ell)}$$

$\Delta_\mathrm{r}\mathrm{V^\infty(aq)}$ is the limiting volume of reaction. We assume that at temperature T, the properties $\mathrm{V_x^\infty(aq)}, \Delta_\mathrm{r}\mathrm{V^\infty(aq)}$ and $\mathrm{V_1^*(\ell)}$ are independent of pressure. Hence using equations (d) and (g) [2,3],

$$\left(\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{p}}\right)_\mathrm{T} = -\mathrm{n_X^0}\,\frac{\left[\Delta_\mathrm{r}\mathrm{V^\infty(aq)}\right]^2}{\mathrm{R\,T}}\,\frac{\mathrm{K^0}}{\left[1+\mathrm{K^0}\right]^2}$$

We have taken account of the fact that,

$$\frac{\mathrm{d\ln\left(K^0\right)}}{\mathrm{dp}} = -\frac{\Delta_\mathrm{r}\mathrm{V^\infty(aq)}}{\mathrm{R\,T}}$$

Similarly [2]

$$\left(\frac{\partial \mathrm{V(aq)}}{\partial \mathrm{T}}\right)_\mathrm{p} = \mathrm{n_X^0}\,\frac{\Delta_\mathrm{r}\mathrm{V^\infty(aq)}\,\Delta_\mathrm{r}\mathrm{H^\infty(aq)}}{\mathrm{R\,T^2}}\,\frac{\mathrm{K^0}}{\left[1+\mathrm{K^0}\right]^2}$$

Equation (h) shows that irrespective of the sign of $\Delta_\mathrm{r}\mathrm{V^\infty(aq)}$, the contribution to $\left(\frac{\partial V(aq)}{\partial p}\right)_\mathrm{T}$ is always negative. No such generalisation emerges with respect to equation (j) [4]. A closely related subject concerns the dependence of rate constants on pressure leading to volumes of activation [5].

Footnotes

[1] From equation (a)

	$X(aq)$	$\Leftrightarrow$	$Y(aq)$	
At $t = 0$,	n_X^0		0	mol
At equilib;	$n_X^0 - \xi$		ξ	mol
In volume V	n_X^0		ξ/V	$molm^{-3}$

[2]

$$dV/dp = [m^3] / [Nm^{-2}] = [m^5\ N^{-1}]$$
$$= \frac{[m^6]}{[Nm]} = [m^5\ N^{-1}]$$

[3]

$$\frac{dV}{dT} = \frac{[m^3]}{[K]}$$
$$n_X^0 \frac{\Delta_r V^\infty(aq)\,\Delta_r H^\infty(aq)}{R\,T^2} \frac{K^0}{[1 + K^0]^2}$$
$$= [mol] \frac{[m^3\ mol^{-1}]\ [Jmol^{-1}]}{[JK^{-1}\ mol^{-1}]\ [K]^2} = [m^3\ K^{-1}]$$

[4] See for example, J. E. Desnoyers, Pure Appl.Chem.,1982, 54,1469.

[5] (i) W. J. leNoble, J. Chem. Educ.,1967,44,729. (ii) B. S. El'yanov and S. D. Hamann, Aust. J Chem.,1975,28,945. (iii) B.S. El'yanov and M. G. Gonikberg, Russian J. Phys. Chem., 1972, 46, 856.

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1.22.2: Volume: Components

One Component

For a system containing one chemical substance we define the volume as follows,

$$V = V\left[T, p, n_1\right]$$

The variables in the square brackets are called the INDEPENDENT VARIABLES. The term independent means that within limits, we can change T independently of the pressure and n_1; change p independently of T and n_1; change n_1 independently of T and p. There are some restrictions in our choice of independent variables. At least one of the variables must define the amount of all chemical substances in the system and one variable must define the degree of 'hotness' of the system.

Two Chemical Substances

If the composition of a given closed system is specified in terms of the amounts of two chemical substances, 1 and 2, four independent variables $[T, p, n_1, n_2]$ define the independent variable V.

$$V = V\left[T, p, n_1, n_2\right]$$

Volume i - Chemical Substances

For a system containing i - chemical substances where the amounts can be independently varied, the dependent variable V is defined by the following equation.

$$V = V\left[T, p, n_1, n_2, \ldots . n_i\right]$$

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1.22.3: Volume: Partial and Apparent Molar

In descriptions of the volumetric properties of solutions, two terms are extensively used. We refer to the partial molar volume of solute j in, for example, an aqueous solution $\mathrm{V}_j(\mathrm{aq})$ and the corresponding apparent molar volume $\phi\,(\mathrm{V}_j)$. Here we explore how these terms are related. We consider an aqueous solution prepared using water, $1\ \mathrm{kg}$, and m_j moles of solute j. The volume of this solution at temperature T and pressure p is given by equation (a).

$$\mathrm{V}\,(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}) = (1/\mathrm{M}_1)\ \mathrm{V}_1(\mathrm{aq}) + \mathrm{m}_\mathrm{j}\,\mathrm{V}_\mathrm{j}(\mathrm{aq})$$

The chemical potential of solvent, water, in the aqueous solution $\mu_1(\mathrm{aq})$ is related to the molality m_j using equation (b) where $\mu_1^*(\ell)$ is the chemical potential of pure water(ℓ), molar mass M_1, at the same T and p.

$$\mu_1(\mathrm{aq}) = \mu_1^*(\ell) - \phi\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m}_\mathrm{j}$$

Here practical osmotic coefficient ϕ is defined by equation (c).

$$\mathrm{limit}\,(\mathrm{m}_\mathrm{j} \to 0)\,\phi = 1 \quad \text{at all T and p}$$

But

$$\mathrm{V}_1(\mathrm{aq}) = [\partial\mu_1(\mathrm{aq})/\partial\mathrm{p}]_\mathrm{T}$$

Then[1]

$$\mathrm{V}_1\,(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}) = \mathrm{V}_1^*(\ell) - \mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m}_\mathrm{j}\,(\partial\phi/\partial\mathrm{p})_\mathrm{T}$$

For the solute, the chemical potential $\mu_j(\mathrm{aq})$ is related to the molality of solute m_j using equation (f) where pressure p is close to the standard pressure.

$$\mu_\mathrm{j}(\mathrm{aq}) = \mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_\mathrm{j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)$$

where

$$\mathrm{limit}\,(\mathrm{m}_\mathrm{j} \to 0)\,\gamma_j = 1 \quad \text{at all T and p}$$

Then[2]

$$\mathrm{V}_\mathrm{j}(\mathrm{aq}) = \mathrm{V}_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\ [\partial\ln(\gamma_\mathrm{j})/\partial\mathrm{p}]_\mathrm{T}$$

$$\mathrm{Limit}\,(m_j \to 0)\,V_j(aq) = V_j^0(aq) = V_j^\infty(aq)$$

Combination of equations (a), (e) and (h) yields equation (j).

$$\begin{aligned}\mathrm{V}\,(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}) = (1/\mathrm{M}_1)\ &[\mathrm{V}_1^*(\ell) - \mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m}_\mathrm{j}\,(\partial\phi/\partial\mathrm{p})_\mathrm{T}] \\ +\mathrm{m}_\mathrm{j}\ &\left\{\mathrm{V}_\mathrm{j}^\infty(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\ [\partial\ln(\gamma_\mathrm{j})/\partial\mathrm{p}]_\mathrm{T}\right\}\end{aligned}$$

An important point emerges if we re-arrange equation (j).

$$\begin{aligned}\mathrm{V}\,(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}) = (1/\mathrm{M}_1)\ &\mathrm{V}_1^*(\ell) \\ +\mathrm{m}_\mathrm{j}\ &\left\{\mathrm{V}_\mathrm{j}^\infty(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\ [\partial\ln(\gamma_\mathrm{j})/\partial\mathrm{p}]_\mathrm{T} - \mathrm{R}\,\mathrm{T}\,(\partial\phi/\partial\mathrm{p})_\mathrm{T}\right\}\end{aligned}$$

Equation (k) has an interesting form in that the brackets {....} contain $\mathrm{V}_\mathrm{j}^\infty(\mathrm{aq})$ and terms describing the extent to which the volumetric properties of the solution are not ideal in a thermodynamic sense. It is therefore convenient to define an apparent molar volume of solute j, $\phi\,(\mathrm{V}_\mathrm{j})$ using equation (l).

$$\phi\,(\mathrm{V}_\mathrm{j}) = \mathrm{V}_\mathrm{j}^\infty(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\ [\partial\ln(\gamma_\mathrm{j})/\partial\mathrm{p}]_\mathrm{T} - \mathrm{R}\,\mathrm{T}\,(\partial\phi/\partial\mathrm{p})_\mathrm{T}$$

Then

$$\mathrm{limit}\,(\mathrm{m}_\mathrm{j} \to 0)\,\phi\,(\mathrm{V}_\mathrm{j}) = \mathrm{V}_\mathrm{j}^\infty(\mathrm{aq})$$

Therefore we obtain equation (n).

$$\mathrm{V}\,(\mathrm{aq};\mathrm{w}_1 = 1\ \mathrm{kg}) = (1/\mathrm{M}_1)\ \mathrm{V}_1^*(\ell) + \mathrm{m}_\mathrm{j}\,\phi\,(\mathrm{V}_\mathrm{j})$$

Interest in equation (n) arises from the fact that the for a given solution $\mathrm{V(aq)}$ can be measured {using the density $\rho(\mathrm{aq})$} and hence knowing $\mathrm{V_1^*}(\ell)$, $\phi\,(\mathrm{V_j})$ is obtained. If we measure $\phi\,(\mathrm{V}_j)$ as a function of m_j, equation (m) indicates how one obtains $\mathrm{V_j^\infty(aq)}$. Moreover the difference $\left[\phi\,(\mathrm{V_j}) - \mathrm{V_j^\infty(aq)}\right]$ signals the role of solute - solute interactions.

Footnotes

[1]

$$\begin{aligned}\mathrm{R\,T}\left[\tfrac{\partial\phi}{\partial \mathrm{p}}\right] &= \left[\mathrm{JK^{-1}\ mol^{-1}}\right]\,[\mathrm{K}]\,\left[\tfrac{1}{[\ \mathrm{N\ m^{-2}}]}\right] \\ &= \left[\mathrm{m^3\ mol^{-1}}\right]\end{aligned}$$

[2]

$$\begin{aligned}\mathrm{R\,T}\left[\frac{\partial \ln(\gamma_\mathrm{j})}{\partial \mathrm{p}}\right] &= \left[\mathrm{JK^{-1}\ mol^{-1}}\right]\,[\mathrm{K}]\,\left[\frac{1}{[\ \mathrm{N\ m^{-2}}]}\right] \\ &= [\mathrm{Nmmol}]\left[\frac{1}{[\ \mathrm{N\ m^{-2}}}\right] = \left[\mathrm{m^3\ mol^{-1}}\right]\end{aligned}$$

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1.22.4: Volume: Partial Molar: Frozen and Equilibrium

Consider the volume of a closed system defined by equation (a).

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}\right]$$

This system is displaced to a neighboring state by addition of a small amount of substance j, $\delta \mathrm{n}_j$. The change in volume at fixed affinity A is related to the change in volume at fixed composition or organization. At fixed temperature, fixed pressure, and fixed n_1,

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_\mathrm{j}}\right)_\mathrm{A} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_\mathrm{j}}\right)_\xi - \left(\frac{\partial \mathrm{A}}{\partial \mathrm{n}_\mathrm{j}}\right)_\xi \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{n}_\mathrm{j}} \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{n}_\mathrm{j}}$$

For a system at equilibrium ($\mathrm{A} = 0$ and $\xi = \xi^{\mathrm{eq}}$), the triple product term on the R.H.S. of equation (b) is not zero. Hence we distinguish between two properties; $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_\mathrm{j}}\right)_{\mathrm{T,p,n_1,\ A=0}}$ and $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_\mathrm{j}}\right)_{\mathrm{T,p,n_1,eq^{eq}}}$. By convention the first of these two terms is called the partial molar volume of substance j in the system.

Example 1

A given aqueous solution is prepared by dissolving n_j moles of urea in n_1 moles of water at $298.2\ \mathrm{K}$ and ambient pressure. This system has volume $\mathrm{V(aq)}$ which is determined in part by water-water, water-urea and urea-urea interactions. We add $\delta \mathrm{n}_j$ moles of urea to this system but stipulate that the water-water, water-urea and urea-urea interactions remain unchanged; i.e. frozen. The property $(\partial \mathrm{V}/\partial \mathrm{n}_\mathrm{j})_{\mathrm{T;p;n(1),}\xi}$ is a frozen partial molar volume of urea in the aqueous solution. On the other hand, if we stipulate that the water-water, water-urea and urea-urea interactions re-adjust in order that the system is at a minimum in Gibbs energy, the property $(\partial \mathrm{V}/\partial \mathrm{n}_\mathrm{j})_{\mathrm{T,p;n(1),A=0}}$ is the equilibrium partial molar volume for urea in this aqueous solution.

Example 2

We consider an aqueous solution containing n_j moles of ethanoic acid in n_1 moles of water at defined temperature and defined pressure. Conventionally, the chemical equilibrium operating in the system is expressed in the following form.

$$\mathrm{HA(aq)} \leftrightarrow \mathrm{H^+(aq)} + \mathrm{A^-(aq)}$$

The volume of this system $\mathrm{V(HA;aq;T;p)}$ is a state variable. We add $\delta\delta\mathrm{(HA)}$ moles of substance HA to the system. In the frozen limit, the amounts of $\mathrm{H^+(aq)}$ and $\mathrm{A^-(aq)}$ in the solution do not change. In terms of composition all that happens is the amount of $\mathrm{HA(aq)}$ increases. Hence, $\left(\frac{\delta \mathrm{V}}{\delta \mathrm{n(HA)}}\right)$ is a measure of the 'frozen partial molar volume' of HA in the system. If we remove the frozen restriction and allow chemical equilibrium to be re-established, the derived quantity is the equilibrium partial molar volume for HA in this aqueous solution, part of added $\delta \mathrm{P}mathrmn\mathrm{(HA)}$ having dissociated in order that the resulting solution has zero affinity for spontaneous change. We use quotation marks '….' Around the phrase 'frozen partial molar volume' to make the point that this property is not a proper equilibrium thermodynamic property.

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1.22.5: Volumes: Solutions: Apparent and Partial Molar Volumes: Determination

An aqueous solution is prepared using n_1 moles of water and n_j moles of solute. Thus,

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}\right]$$

The density of this solution $\rho(\mathrm{aq})$ can be accurately measured at the specified temperature and pressure together with the density of the pure solvent, $\rho_1^*(\ell)$. The molar mass of the solute is M_j kgmol^{-1}. Two equations [1-3] are encountered in the literature depending on the method used to describe the composition of the solution [4]. Molality Scale [1]

$$\phi\left(V_j\right) = \left[m_j\, \rho(\mathrm{aq})\, \rho_1^*(\ell)\right]^{-1}\, \left[\rho_1^*(\ell) - \rho(\mathrm{aq})\right] + \mathrm{M_j}/\rho(\mathrm{aq})$$

Concentration Scale [2,3]

$$\phi\left(\mathrm{V_j}\right) = \left[\mathrm{c_j}\, \rho_1^*(\ell)\right]^{-1}\, \left[\rho_1^*(\ell) - \rho(\mathrm{aq})\right] + \mathrm{M_j}/\rho_1^*(\ell)$$

Equation (b) using molalities and (c) using concentrations yield the same property of the solute, namely the apparent molar volume of solute j, $\phi\left(\mathrm{V}_j\right)$. Equations (b) and (c) are exact. The equations are readily distinguished by the difference in the denominators of the last terms. In any event the trick in deriving these equations is to seek an equation having the form, {[Property of solvent] minus [Property of solute]}.

The subject is slightly complicated because the concentration of solute j can be expressed using either the unit 'molm^{-3}' or the unit 'moldm^{-3}', the latter being the most common. There is also a problem over the unit used for densities. Some authors use the unit 'kgm^{-3}' whereas other authors use the unit 'gcm^{-3}'. The latter practice accounts for the numerical factor 10^3 which often appears in many published equations of the form shown in equations (b) and (c).

Partial molar and partial molal properties are often identified. The two terms are synonymous in the case of partial molar volumes and partial molal volumes of solutes in aqueous solutions. IUPAC recommends the use of the term 'partial molar volume' [5].

Significantly we can never know the absolute value of the chemical potential of a solute in a given solution but we can determine the partial molar volume, the differential dependence of chemical potential on pressure. Indeed the challenge of understanding patterns in partial molar volumes seems less awesome than the task of understanding other thermodynamic properties of solutes.

Equations (b) and (c) do not describe how $\phi\left(\mathrm{V}_j\right)$ for a given solute depends on either m_j or c_j. This dependence is characteristic of a solute (at fixed T and p) and reflects the role of solute - solute interactions. In many cases where solute j is a simple neutral solute, $\phi\left(\mathrm{V}_j\right)$ for dilute solutions is often satisfactorily accounted for by an equation in which $\phi\left(\mathrm{V}_j\right)$ is a linear function of m_j. The slope S is characteristic of the solute (at fixed T and p) [4d,6].

$$\phi\left(V_j\right) = \phi\left(\mathrm{V_j}\right)^\infty + \mathrm{S}\, \left(\mathrm{m_j}/\mathrm{m}^0\right)$$

$$\mathrm{limit}\left(\mathrm{m_j} \to 0\right) \phi\left(\mathrm{V_j}\right) = \phi\left(\mathrm{V_j}\right)^\infty = \mathrm{V_j^\infty(aq)}$$

In the case of urea(aq) at 298.2 K and ambient pressure the dependence of $\phi\left(\mathrm{V}_j\right)$ on m_j is described by the following quadratic equation [7,8].

$$\phi\left(\mathrm{V_j}\right)/\mathrm{cm}^3\ \mathrm{mol}^{-1} = 44.20 + 0.126\, \left(\mathrm{m_j}/\mathrm{m}^0\right) - 0.004\, \left(\mathrm{m_j}/\mathrm{m}^0\right)^2$$

In general terms therefore $\mathrm{V_j^\infty(aq)}$ {and $\mathrm{V_j^\infty}$ for solute j in other solvents [9]} characterizes solute - solvent interactions and the dependences of $\mathrm{V_j(aq)}$ on m_j characterizes solute - solute interactions. Of course the partial molar volume of solute-j in solution is **not** the actual volume of solute-j. Instead $\mathrm{V_j(aq;T;p)}$ measures the differential change in the volume of an aqueous solution when $\delta \mathrm{n}_j$ moles of substance-j are added. We emphasize the importance of an approach using the molalities of solutes. The reasons are straightforward. If we compare $\phi\left(\mathrm{V}_j\right)$ for a solute in solutions containing 0.1 and 0.01 molkg^{-1}, in this comparison, the mass of solvent remains the same. If on the other hand we compare $\phi\left(\mathrm{V}_j\right)$ for solute in solutions where $\mathrm{c}_j/\ \mathrm{moldm}^{-3} = 0.1$ and 0.01, the amounts of solvent are not defined. Nevertheless many treatments of the properties of solutions examine $\phi\left(\mathrm{V}_j\right)$ as a function of concentration. In fact chemists tend to think in terms of concentrations and hence in terms of distances between solute molecules. So in these terms concentration might be thought of as the 'natural' scale. Just as in life, one is more interested in the distance between two people rather than their mass. No rule forbids one to fit the dependences of $\phi\left(\mathrm{V}_j\right)$ on c_j using an equation of the following form.

$$\phi\left(V_j\right) = a_1 + a_2\, c_j + a_3\, c_j^2 + \ldots$$

But if $\phi\left(\mathrm{V_j}\right)$ is a linear function of m_j, $\phi\left(\mathrm{V}_j\right)$ is not a linear function of c_j [10]. Of course $\phi\left(\mathrm{V_j}\right) = \phi\left(\mathrm{V_j}\right)^{\infty}$ in both $\mathrm{limit}\left(\mathrm{m}_j \to 0\right)$ and $\mathrm{limit}\left(\mathrm{c}_j \to 0\right)$.

Granted the outcome of an experiment is the dependence of $\phi\left(\mathrm{V}_j\right)$ on m_j, the partial molar volume $\mathrm{V_j(aq)}$ of solute j is readily calculated; equation (h) [11].

$$\mathrm{V_j(aq)} = \phi\left(\mathrm{V_j}\right) + \mathrm{m_j}\left(\frac{\partial\phi\left(\mathrm{V_j}\right)}{\partial \mathrm{m_j}}\right)$$

We note important features in the context of two plots;

i. $\mathrm{V\left(aq; w_1/kg = 1\right)}$ and

1. $\left[\mathrm{V\left(aq; w_1 = 1\ kg\right)} - \left(1/\mathrm{M_1}\right)\ \mathrm{V_1^*}(\ell)\right]$ against molality m_j.

Then $\mathrm{V}_j(\mathrm{aq})$ is the gradient of the tangent to the curve in plot (i) at the specified molality; $\phi\left(\mathrm{V}_j\right)$ is the gradient of the line in plot(ii) joining the origin and $\left[\mathrm{V\left(aq; w_1 = 1\ kg\right)} - \left(1/\mathrm{M_1}\right)\ \mathrm{V_1^*}(\ell)\right]$ at the specified molality.

Footnotes

[1] For the solution volume $\mathrm{V(aq)}$,

$$\mathrm{V(aq)} = \mathrm{n_1\, V_1^*}(\ell) + \mathrm{n_j}\,\phi\left(\mathrm{V_j}\right)$$

If the molar mass of the solvent is $\mathrm{M_1\ kgmol^{-1}}$, $\mathrm{V(aq)} = \left[\mathrm{n_1\, M_1 + n_j\, M_j}\right]/\rho\mathrm{(aq)}$ and $\mathrm{V_1^*}(\ell) = \mathrm{M_1}/\rho_1^*(\ell)$. From equation (a),

$$\frac{\mathrm{n_1\, M_1}}{\rho\mathrm{(aq)}} + \frac{\mathrm{n_j\, M_j}}{\rho\mathrm{(aq)}} = \mathrm{n_1}\,\frac{\mathrm{M_1}}{\rho_1^*(\ell)} + \mathrm{n_j}\,\phi\left(\mathrm{V_j}\right)$$

Divide by $\mathrm{n_1\ \ M_1}$ and rearrange;

$$\frac{n_j}{n_1\, M_1}\,\phi\left(V_j\right) = \frac{1}{\rho(aq)} - \frac{1}{\rho_1^*(\ell)} + \frac{n_j\, M_j}{n_1\, M_1\, \rho(aq)}$$

But molality $\mathrm{m_j} = \mathrm{n_j}/\mathrm{n_1\, M_1}$. Then,

$$\mathrm{m_j}\,\phi\left(\mathrm{V_j}\right) = \left[\frac{1}{\rho\mathrm{(aq)}} - \frac{1}{\rho_1^*(\ell)}\right] + \frac{\mathrm{m_j\, M_j}}{\rho\mathrm{(aq)}}$$

or,

$$\phi\left(V_j\right) = \left[m_j\,\rho(aq)\,\rho_1^*\right]^{-1}\ \left[\rho_1^*(\ell) - \rho(aq)\right] + \frac{M_j}{\rho(aq)}$$

Thus,

$$\phi\left(\mathrm{V_j}\right) = \left[\frac{1}{\left[\ \mathrm{mol\ kg^{-1}}\right]\ \left[\mathrm{kgm^{-3}}\right]^2}\right]\ \left[\mathrm{kgm^{-3}}\right] + \frac{\left[\mathrm{kgmol^{-1}}\right]}{\left[\mathrm{kgm^{-3}}\right.} = \left[\mathrm{m^3\ mol^{-1}}\right]$$

[2] At fixed T and p,

$$\mathrm{c_j} = \mathrm{n_j}/\mathrm{V(aq)} = \mathrm{n_j}/\left[\mathrm{n_1\, V_1^*(l) + n_j}\,\phi\left(\mathrm{V_j}\right)\right]$$

But, $\mathrm{m_j} = \mathrm{n_j}/\mathrm{n_l\, M_1}$. Then,

$$\mathrm{c_j} = \frac{\mathrm{m_j\, n_1\, M_1}}{\mathrm{n_1\, V_1^*}(\ell) + \mathrm{n_j}\,\phi\left(\mathrm{V_j}\right)}$$

Invert. $\frac{1}{\mathrm{c_j}} = \frac{\mathrm{n_1\, V_1^*}(\ell)}{\mathrm{m_j\, n_1\, M_1}} + \frac{\mathrm{n_j}\,\phi\left(\mathrm{V_j}\right)}{\mathrm{m_j\, n_1\, M_1}}$ But $\mathrm{n_j/m_j\, n_1\, M_1} = 1$ Then,

$$\frac{1}{\mathrm{c_j}} = \frac{1}{\mathrm{m_j}\,\rho_1^*(\ell)} + \phi\left(\mathrm{V_j}\right)$$

or,

$$\frac{1}{\mathrm{m_j}} = \frac{\rho_1^*(\ell)}{\mathrm{c_j}} - \rho_1^*(\ell)\,\phi\,(\mathrm{V_j})$$

The latter equation links m_j and c_j.

[3] From [1],

$$\phi\,(\mathrm{V_j}) = \frac{1}{\mathrm{m_j}}\left[\frac{1}{\rho(\mathrm{aq})} - \frac{1}{\rho_1^*(\ell)}\right] + \frac{\mathrm{M_j}}{\rho(\mathrm{aq})}$$

Then, from [2],

$$\phi\,(V_j) = \left[\frac{\rho_1^*(\ell)}{c_j} - \rho_1^*(\ell)\,\phi\,(V_j)\right]\left[\frac{1}{\rho(\mathrm{aq})} - \frac{1}{\rho_1^*(\ell)}\right] + \frac{M_j}{\rho(\mathrm{aq})}$$

Hence,

$$\phi\,(\mathrm{V_j}) = \frac{\rho_1^*(\ell)}{\mathrm{c_j}\,\rho(\mathrm{aq})} - \frac{1}{\mathrm{c_j}} - \frac{\rho_1^*(\ell)\,\phi\,(\mathrm{V_j})}{\rho(\mathrm{aq})} + \phi\,(\mathrm{V_j}) + \mathrm{M_j}/\rho(\mathrm{aq})$$

Then, $\phi\,(\mathrm{V_j})\ \frac{\rho_1^*(\ell)}{\rho(\mathrm{aq})} = \frac{\rho_1^*(\ell)}{\mathrm{c_j}\,\rho(\mathrm{aq})} - \frac{1}{\mathrm{c_j}} + \frac{\mathrm{M_j}}{\rho(\mathrm{aq})}$

$$\phi\,(\mathrm{V_j}) = \frac{1}{\mathrm{c_j}} - \frac{1}{\mathrm{c_j}}\,\frac{\rho(\mathrm{aq})}{\rho_1^*(\ell)} + \frac{\mathrm{M_j}}{\rho_1^*(\ell)}$$

or,

$$\phi\,(\mathrm{V_j}) = [\mathrm{c_j}\,\rho_1^*(\ell)]^{-1}\ [\rho_1^*(\ell) - \rho(\mathrm{aq})] + \mathrm{M_j}/\rho_1^*(\ell)$$

Thus,

$$\phi\,(\mathrm{V_j}) = \frac{1}{[\ \mathrm{mol\ m^{-3}}]}\,\frac{1}{[\ \mathrm{kg\ m^{-3}}]^{-1}}\ [\mathrm{kgm^{-3}}] + \frac{[\mathrm{kgmol^{-1}}]}{[\mathrm{kgm^{-3}}]} = [\mathrm{m^3\ mol^{-1}}]$$

[4] The following publications use equation (b) based on the molality composition scale.

a. Dipeptides(aq); J. E. Reading, I. D. Watson and G .R. Hedwig, J. Chem. Thermodyn., 1990, **22**, 159.
b. N-alkoxyethanols(aq); G. Roux, G. Peron and J. E. Desnoyers, J. Solution Chem.,1978,**7**,639.
c. Cyclic organic chemical substhances in 1-ocytanol; P. Berti, S. Cabani and V. Mollica, Fluid Phase Equilib.,1987,**32**,195.
d. Alkali halides in urea + water; N. Desrosiers, G. Perron, J. G. Mathieson, B. E. Conway and J. E. Desnoyers, J. Solution Chem.,1974,3,789.
e. HCl(aq), HBr(aq) and HI(aq); T. M. Herrington, A.D. Pethybridge and M. G. Roffey, J. Chem. Eng. Data,1985,**30**,264.
f. LiOH(aq), NaOH(aq), KOH(aq); T. M. Herrington, A.D. Pethybridge and M. G. Roffey, J. Chem. Eng. Data,1986,**31**,31.
g. $\mathrm{R_4NI(aq)}$;B. M. Lowe and H. M. Rendall, Trans. Faraday Soc.,1971,**67**,2318.
h. HCl(aq) and $\mathrm{HClO_4(aq)}$; R. Pogue and G. Atkinson, J. Chem. Eng. Data, 1988,**33**,495.
i. $\mathrm{MCl_2(aq)}$ where M= Mn, Co, Ni, Zn and Cd; T. M. Herrington, M. G. Roffey, and D. P. Smith, J. Chem.Eng. Data,1986,**31**,221.
j. $\mathrm{NiCl_2(aq),\ Ni\,(ClO_4)_2\,(aq),\ CuCl_2(aq)\ and\ Cu\,(ClO_4)_2\,(aq)}$; R. Pogue and G. Atkinson, J. Chem. Eng. Data, 1988,**33**,370.
k. $\mathrm{RMe_3NBr(aq)}$; R. De Lisi, S. Milioto and R. Triolo, J. Solution Chem.,1988,**17**,673.
l. $\mathrm{Ph_4AsCl(aq)}$; F. J. Millero, J. Chem. Eng. Data, 1971,**16**,229.
m. $\mathrm{R_4NBr(aq + BuOH)}$; L. Avedikian, G. Perron and J. E. Desnoyers, J. Solution Chem.,1975,**4**,331.

Applications of equation. (c) include

a. $\mathrm{Bu_4N^+\ carboxylates(aq)}$; P.-A.Leduc, and J. E. Desnoyers, Can. J. Chem.,1973,**51**,2993.
b. N-Alkylamine hydrobromides(aq); P.-A.Leduc, and J. E. Desnoyers, J. Phys. Chem., 1974, **78**, 1217.
c. $\mathrm{R_4N^+\ Cl^-(aq + DMSO)}$; D. D. Macdonald and J.B.Hyne, Can. J.Chem.,1970,**48**,2416.
d. $\mathrm{R_4N^+\ Cl^-(aq + EtOH)}$; I. Lee and J. B. Hyne, Can. J.Chem.,1968,**46**,2333.

[5] Manual of Symbols and Terminology for Physicochemical Quantities and Units, IUPAC, Pergamon, Oxford, 1979.

[6] F. Franks and H.T. Smith, Trans. Faraday Soc., 1968, **64**, 2962.

[7] D. Hamilton and R. H. Stokes, J. Solution Chem., 1972,**1**, 213.

[8] R. H. Stokes, Aust . J. Chem., 1967,**20**, 2087.

[9]

Solvent	V^{infty} (urea; sln; 298 K; ambient p)/cr mol^{-1}
H_2O	44.24
CH_3OH	36.97
C_2H_5OH	40.75
Formamide	44.34
DMF	39.97
DMSO	41.86

[10] From [2], $m_j = c_j / [\rho_1^*(\ell) - \rho_1^*(\ell)\, \phi\,(V_j)\; c_j]$. If $\phi\,(V_j) = a_1 + a_2\, m_j$ Then,

$$\phi\,(V_j) = a_1 + \{a_2/\rho_1^*(\ell)\; [1 - \phi\,(V_j)\; c_j]\}\; c_j$$

i.e. the slope depends on the product $\phi\,(V_j)\; c_j$.

[11] From

$$V(aq) = n_1\, V_1^*(\ell) + n_j\, \phi\,(V_j)$$

At constant n_1,

$$\left(\frac{\partial V}{\partial n_j}\right) = \phi\,(V_j) + n_j \left(\frac{\partial \phi\,(V_j)}{\partial n_j}\right)$$

Or,

$$V_j = \phi\,(V_j) + m_j \left(\frac{\partial \phi\,(V_j)}{\partial m_j}\right)$$

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1.22.6: Volumes: Apparent Molar and Excess Volumes

For a solution prepared using $1\ \mathrm{kg}$ of water, the volume is related to the apparent molar volume of the solute $\phi\left(\mathrm{V}_j\right)$ using equation (a).

$$\mathrm{V}\left(\mathrm{aq}; \mathrm{w}_1 = 1\ \mathrm{kg}\right) = \left(1/\mathrm{M}_1\right)\ \mathrm{V}_1^*(\ell) + \mathrm{m}_\mathrm{j}\,\phi\left(\mathrm{V}_\mathrm{j}\right)$$

If the thermodynamic properties of this solution are ideal,

$$\mathrm{V}\left(\mathrm{aq}; \mathrm{id}; \mathrm{w}_1 = 1\ \mathrm{kg}\right) = \left(1/\mathrm{M}_1\right)\ \mathrm{V}_1^*(\ell) + \mathrm{m}_\mathrm{j}\,\phi\left(\mathrm{V}_\mathrm{j}\right)^\infty$$

Here $V_\mathrm{j}^\infty(\mathrm{aq}) \equiv \phi\left(\mathrm{V}_\mathrm{j}\right)^\infty$. The difference between $\mathrm{V}(\mathrm{aq})$ and $\mathrm{V}(\mathrm{aq:id})$ defines an excess volume $\mathrm{V}^\mathrm{E}\left(\mathrm{aq}; \mathrm{w}_1 = 1\ \mathrm{kg}\right)$. Thus,

$$\mathrm{V}^\mathrm{E}\left(\mathrm{aq}; \mathrm{w}_1 = 1\ \mathrm{kg}\right) = \mathrm{V}\left(\mathrm{aq}; \mathrm{w}_1 = 1\ \mathrm{kg}\right) - \mathrm{V}\left(\mathrm{aq}; \mathrm{w}_1 = 1\ \mathrm{kg} : \mathrm{id}\right)$$

Hence,

$$\mathrm{V}^\mathrm{E}\left(\mathrm{aq}; \mathrm{w}_1 = 1\ \mathrm{kg}\right) = \mathrm{m}_\mathrm{j}\ \left[\phi\left(\mathrm{V}_\mathrm{j}\right) - \phi\left(\mathrm{V}_\mathrm{j}\right)^\infty\right]$$

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1.22.7: Volumes: Neutral Solutes: Limiting Partial Molar Volumes

A given aqueous solution at temperature T and pressure p contains solute j, having molality m_j. The chemical potential of solute j, $\mu_j(\mathrm{aq})$ is related to m_j using equation (a).

$$\mu_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{0}\left(\mathrm{aq};\mathrm{T};\mathrm{p}^{0}\right) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_{\mathrm{j}}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right) + \int_{\mathrm{p}^{0}}^{\mathrm{p}} \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T})\,\mathrm{dp}$$

But

$$\mathrm{V}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \left(\frac{\partial \mu_{\mathrm{j}}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

Also $\mu_{\mathrm{j}}^{0}\left(\mathrm{aq};\mathrm{T};\mathrm{p}^{0}\right)$ is, by definition, independent of pressure. From equation (a),

$$\mathrm{V}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) + \mathrm{R}\,\mathrm{T}\left(\frac{\partial \ln\left(\gamma_{\mathrm{j}}\right)}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

In equation (c), there is no term explicitly in terms of molaity m_j. From the definition of γ_j,

$$\text{limit}\,(\mathrm{m}_{\mathrm{j}} \to 0)\,\mathrm{V}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p})$$

$\mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p})$ is the limiting partial molar volume of solute j in aqueous solution at temperature T and pressure p. In other words $\mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p})$ is the partial molar volume of solute j in the (ideal) solution where there are no solute-solute interactions and characterizes solute-water interactions. Because γ_j tends to unity as m_j tends to zero, γ_j is sometimes called an asymmetric activity coefficient [1]. [Contrast rational activity coefficients where $\mathrm{f}_1 \to 1$ as $\mathrm{x}_1 \to 1$.]

At the risk of being repetitive we distinguish between the two possible reference states for substance j such as urea. One reference state is the pure solid chemical substance j at ambient pressure and 298.2 K. Another reference state is the ideal solution where $\mathrm{m}_{\mathrm{j}} = 1\ \mathrm{mol\ kg^{-1}}$ at ambient pressure and 298.2 K. The properties of urea in the two states, pure solid and solution standard state are clearly quite different. Indeed, we can compare $\mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};298.2\ \mathrm{K};\ \text{ambient p})$ and $\mathrm{V}_{\mathrm{j}}^{*}(\ \mathrm{s};298.2\ \mathrm{K};\ \text{ambient p})$. We can also compare, for example, $\mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{j}\ =\ \text{urea};\ \mathrm{sln}298.2\ \mathrm{K};\ \text{ambient p})$ in a range of solvents [2]. These points are also nicely illustrated by the volumetric properties of water [3,]. At 298.2 K and ambient pressure $\mathrm{V}_1^{*}(\ell;\mathrm{H_2O})$ is $18.07\ \mathrm{cm^3\ mol^{-1}}$ but for water as a solute in three solvents, $\mathrm{V}^{\infty}\left(\mathrm{H_2O};\mathrm{sln}\right) = 18.47(\mathrm{MeOH}), 14.42(\mathrm{EtOH})\ \text{and}\ 17.00(\mathrm{THF})\mathrm{cm^3\ mol^{-1}}$ [4]. There is, of course, no reason why we should expect anything different. A water molecule in liquid water is surrounded by many millions of other water molecules. But a water molecule at infinite dilution in solvent ethanol is surrounded by many millions of ethanol molecules [5,6].

In the analysis of experimental results , we may express the composition of the solution in terms of mole fraction of solute x_j. Then

$$\mu_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{0}\left(\mathrm{aq};\mathrm{T};\mathrm{p}^{0};\mathrm{x}-\mathrm{scale}\right) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{x}_{\mathrm{j}}\,\mathrm{f}_{\mathrm{j}}^{*}\right) + \int_{\mathrm{p}^{0}}^{\mathrm{p}} \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T})\,\mathrm{dp}$$

But mole fraction x_j is independent of pressure.

$$\mathrm{V}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) + \mathrm{R}\,\mathrm{T}\left(\frac{\partial \ln\left(\mathrm{f}_{\mathrm{j}}^{*}\right)}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

From the definition of $\mathrm{f}_{\mathrm{j}}^{*}$,

$$\text{limit}\,(\mathrm{x}_{\mathrm{j}} \to 0)\,\mathrm{V}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{V}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p})$$

The limiting value of $\mathrm{V}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p})$ is identical on the molality and mole fraction scales. If we use the concentration scale a problem arises in that the concentration of solute j, c_j is dependent on pressure because the volume of the solution is pressure dependent.

Footnote

[1] W. L. Masterton and H. K. Seiler, J. Phys. Chem., 1968,**72**, 4257.

[2] For j = urea at 298.2 K and ambient pressure, $V_j^{\infty}(\mathrm{sln})/\mathrm{cm}^3\ \mathrm{mol}^{-1}$ = 44.24 (water), 36.97 (methanol), 40.75 (ethanol) and 41.86 (DMSO).

[3] $V_j^{\infty}(298.15\ \mathrm{K; j = water}) = 18.57\ \mathrm{cm}^3\ \mathrm{mol}^{-1}(\mathrm{solvent = octan\text{-}1\text{-}ol})$ and $31.3\mathrm{cm}^3\ \mathrm{mol}^{-1}\ (\mathrm{solvent} = CCl_4)$; P. Berti, S. Cabani and V. Mollica, Fluid PhaseEquilib., 1987,**32** , 1.

[4] M. Sakurai and T. Nakagawa, Bull. Chem. Soc. Jpn., 1984, **55**, 195; J. Chem. Thermodyn., 1982, **14**, 269; 1984, **16** , 171.

[5] A similar contrast exists (H. Itsuki, S. Terasawa, K. Shinohara and H. Ikezwa, J. Chem. Thermodyn., 1987,**19**, 555) between the molar volume of a hydrocarbon and its limiting partial molar volume in another hydrocarbon; $V^*(\ell; C_6H_{14}) = 131.61\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$, but $V^{\infty}(C_6H_{14};\ \mathrm{sln;\ solvent} = C_{16}H_{34}) = 130.2\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ at 298 K and ambient pressure.

In this context the limiting enthalpies of solution water in monohydric alcohols depend on the alcohol at 298.2 K; (S.-O. Nilsson, J. Chem. Thermodyn., 1986, **18**, 1115).

[6] The partial molar volumes of fullerene in solution is $401\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ in *cis*-decalin and Extra close brace or missing open brace in 1,2-dichlorobenzene both values being significantly less than the predicted volume of the pure liquid C_{60}; (P. Ruelle, A. Farina-Cuendet and U. W. Kesselring, J. Chem. Soc. Chem. Commun., 1995, 1161).

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1.22.8: Volume: Salt Solutions: Born-Drude-Nernst Equation

Differentiation of the Born Equation with respect to pressure (at fixed temperature) yields the Born-Drude-Nernst Equation which describes the difference in partial molar volumes of ion j in the gas phase and in solution. The simplest model assumes that the radius r_j is independent of pressure [1].

$$\Delta(\mathrm{pfg} \rightarrow \mathrm{s\,ln})\mathrm{V_j}\left(\mathrm{c_j} = 1\ \mathrm{moldmm^{-3}}; \mathrm{id}; \mathrm{p}, \mathrm{T}\right) = -\mathrm{N_A}\ (\mathrm{z_j\,e})^2 \left[\frac{1}{\varepsilon_\mathrm{r}}\left(\frac{\partial \varepsilon_\mathrm{r}}{\partial \mathrm{p}}\right)_\mathrm{T}\right] \frac{1}{8\,\pi\,\mathrm{r_j}\,\varepsilon_0}$$

A more complicated equation emerges if radius r_j is assumed to depend on pressure, but there seems little merit in taking account of such a dependence.

Footnote

[1]

$$\left[\mathrm{m^3\ mol^{-1}}\right] = \left[\mathrm{mol^{-1}}\right]\ \left[\mathrm{A^2\ s^2}\right]\ \left[\mathrm{Nm^{-2}}\right]^{-1}\ [1]^{-1}\,[1]^{-1}\ \left[\mathrm{m^{-1}}\right]\ \left[\mathrm{Fm^{-1}}\right]^{-}$$

where, $\left[\mathrm{Fm^{-1}}\right] = \left[\mathrm{A^2\ s^4\ kg^{-1}\ m^{-3}}\right]$

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1.22.9: Volume: Liquid Mixtures

A given binary liquid mixture is prepared using n_1 moles of liquid 1 and n_2 moles of liquid 2 at temperature T and pressure p. The term 'mixture' usually means that a homogeneous single liquid phase is spontaneously formed on mixing characterized by a minimum in Gibbs energy G where the molecular organization is characterized by ξ^{eq}. $\mathrm{G}_{\mathrm{m}}^{\mathrm{E}}$ measures the extent to which $\mathrm{G}/\left(\mathrm{n}_1+\mathrm{n}_2\right)$ differs from this ratio in the event that the mixing is, in a thermodynamic sense, ideal.

A given binary liquid mixture is displaced to a neighboring state by a change in pressure at constant temperature. The overall composition remains at $\left(\mathrm{n}_1+\mathrm{n}_2\right)$ but the organization changes to a new value for ξ^{eq} where '$\mathrm{A}=0$'. The differential dependence of $\mathrm{G}_{\mathrm{m}}^{\mathrm{E}}$ on pressure at constant temperature T is the excess molar volume $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$.

$$\mathrm{V}(\mathrm{mix})=\left(\frac{\partial \mathrm{G}(\mathrm{mix})}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0}$$

$$\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}=\left(\frac{\partial \mathrm{G}_{\mathrm{m}}^{\mathrm{E}}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0}$$

For the molar volume,

$$\mathrm{V}_{\mathrm{m}}=\left(\frac{\partial \mathrm{G}_{\mathrm{m}}}{\partial \mathrm{p}}\right)_{\mathrm{T,A}=0}$$

The quantities, $\mathrm{V}(\mathrm{mix})$, V_{m} and $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ are interesting because they can be determined [1] whereas the same cannot be said for $\mathrm{G}(\mathrm{mix})$ and G_{m} although $\mathrm{G}_{\mathrm{m}}^{\mathrm{E}}$ can be obtained m from vapor pressures of mixtures and pure components.

$$\mathrm{V}_{\mathrm{m}}=\mathrm{V}(\mathrm{mix})/\left(\mathrm{n}_1+\mathrm{n}_2\right)$$

Density,

$$\rho(\mathrm{mix})=\left(\mathrm{n}_1 \mathrm{M}_1+\mathrm{n}_2 \mathrm{M}_2\right)/\mathrm{V}(\mathrm{mix})$$

M_1 and $\mathrm{M}_2 are the molar masses of the two liquid components. By measuring \(\rho(\mathrm{mix})$ as a function of mixture composition, we form a plot of molar volume Vm as a function of mole fraction composition. The plot has two limits;

$$\text{limit}\left(\mathrm{x}_1 \rightarrow 1\right) \mathrm{V}_{\mathrm{m}}=\mathrm{V}_1^*(\ell)$$

$$\text{limit}\left(\mathrm{x}_2 \rightarrow 1\right) \mathrm{V}_{\mathrm{m}}=\mathrm{V}_2^*(\ell)$$

If the thermodynamic properties of the binary liquid mixture are ideal (i.e. $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}=0$),

$$\mathrm{V}_{\mathrm{m}}(\mathrm{id})=\mathrm{x}_1 \mathrm{V}_1^*(\ell)+\mathrm{x}_2 \mathrm{V}_2^*(\ell)$$

Or,

$$\mathrm{V}_{\mathrm{m}}(\mathrm{id})=\left(1-\mathrm{x}_2\right) \mathrm{V}_1^*(\ell)+\mathrm{x}_2 \mathrm{V}_2^*(\ell)$$

Hence,

$$\mathrm{V}_{\mathrm{m}}(\mathrm{id})=\mathrm{V}_1^*(\ell)+\mathrm{x}_2\left[\mathrm{V}_2^*(\ell)-\mathrm{V}_1^*(\ell)\right]$$

The latter is an equation for a straight line. The molar volume of a real binary liquid mixture is usually less than $\mathrm{V}_m(\mathrm{id})$. For a real binary liquid mixture,

$$\mathrm{V}_{\mathrm{m}}(\mathrm{mix})=\mathrm{x}_1 \mathrm{V}_1(\mathrm{mix})+\mathrm{x}_2 \mathrm{V}_2(\mathrm{mix})$$

The difference between the molar volume of real and ideal binary liquid mixture is the excess molar volume $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$.

$$\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}=\mathrm{x}_1\left[\mathrm{V}_1(\mathrm{mix})-\mathrm{V}_1^*(\ell)\right]+\mathrm{x}_2\left[\mathrm{V}_2(\mathrm{mix})-\mathrm{V}_2^*(\ell)\right]$$

Or,

$$V_m^E=x_1 V_1^E(\mathrm{mix})+x_2 V_2^E(\mathrm{mix}$$

A given mixture, mole fraction x_2 at temperature T and pressure p, is perturbed by addition of δn_2 moles of chemical substance 2. The system can be perturbed either at constant organization ξ or constant affinity A. Here we are concerned with $\left(\frac{\partial V}{\partial n_2}\right)_{T,p,n(1),A=0}$, the (equilibrium) partial molar volume of substance 2 in the mixture, $V_2(mix)$.The condition '$A = 0$' implies that there is a change in organization ξ in order to hold the system in the equilibrium state. A similar argument is formulated for the (equilibrium) partial molar volume $V_1(mix)$. Moreover according to the Gibbs-Duhem equation (at constant temperature and pressure),

$$n_1\, d\, V_1(mix) + n_2\, d\, V_2(mix) = 0$$

Further,

$$V(mix) = n_1\, V_1(mix) + n_2\, V_2(mix)$$

The property $V(mix)$ is directly determined from the density $\rho(mix)$.

$$V(mix) = (n_1\, M_1 + n_2\, M_2)\, /\rho(mix)$$

The important point is that the thermodynamic extensive property $V(mix)$ is directly determined by experiment whereas we cannot for example measure the enthalpy $H(mix)$. The excess molar volume is given by equation (l).

$$\begin{aligned}\frac{dV_m^E}{dx_1} =& [V_1(mix) - V_1^*(\ell)] + x_1\, \frac{dVV_1(mix)}{dx_1} \\ & - [V_2(mix) - V_2^*(\ell)] + x_2\, \frac{dV_2(mix)}{dx_1}\end{aligned}$$

Using the Gibbs -Duhem equation,

$$\frac{dV_m^E}{dx_1} = [V_1(mix) - V_1^*(\ell)] - [V_2(mix) - V_2^*(\ell)]$$

Or,

$$[V_1(mix) - V_1^*(\ell)] = \frac{dV_m^E}{dx_1} + [V_2(mix) - V_2^*(\ell)]$$

From equation (l),

$$V_m^E = x_1\, \frac{dV_m^E}{dx_1} + x_1\, [V_2(mix) - V_2^*(\ell)] + x_2\, [V_2(mix) - V_2^*(\ell)]$$

Hence,

$$[V_2(mix) - V_2^*(\ell)] = V_m^E - x_1\, \frac{dV_m^E}{dx_1}$$

The derivation leading up to equation (s) is the 'Method of Tangents'. Moreover at the mole fraction composition where $\frac{dV_m^E}{dx_1}$ is zero, $[V_2(mix) - V_2^*(\ell)]$ equals V_m^E.

For liquid component 1 the chemical potential in the liquid mixture is related to the mole fraction composition (at temperature T and pressure p).

$$\mu_1(mix, T, p) = \mu_1^*(\ell, T) + R\, T\, \ln(x_1\, f_1) + \int_{p^0}^{p} V_1^*(\ell; T)\, dp$$

At temperature T and pressure p,

$$V_1(mix) = V_1^*(\ell) + R\, T\, [\partial \ln(f_1)\, /\partial p]_T$$

But

$$V_1^E(mix) = V_1(mix) - V_1^*(\ell)$$

Hence,

$$V_1^E(mix) = R\, T\, [\partial \ln(f_1)\, /\partial p]_T$$

Then,

$$V_m^E(mix) = R\,T\,\{x_1\,[\partial \ln(f_1)/\partial p]_T + x_2\,[\partial \ln(f_2)/\partial p]_T\}$$

Footnote

[1] R. Battino, Chem.Rev.,1971,**71**,5.

[2]

a. C_mH_{2m+2} as a solute in C_nH_{2n+2} solvent; H. Itsuki, S. Terasowa, K. Shinora and H. Ikezawa, J Chem. Thermodyn.,19897,**19**,555.
b. 60[Fullerene} in apolar solvents; P. Ruella, A. Farina-Cuendet and U.W. Kesselring, J. Chem. Soc. Chem. Commun.,1995,1161.

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SECTION OVERVIEW

1.23: Water

Topic hierarchy

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1.23.2: Water: Molar Volume

1.23.3: Water: Hydrogen Ions

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1.23.1: Water

There can be little doubt that water(ℓ) has been all-pervasive in the development of thermodynamics and, of course, solution chemistry. Chemical laboratories throughout the whole world have this liquid ‘on tap’. Speculation about intelligent life forms (cf. are we alone?) in the rest of the universe [1] often start with comments concerning the presence of water(ℓ) on distant planets.

Footnotes

[1] Bill Bryson, A Short History of Nearly Everything, Doubleday, New York, 2003, chapter 16.

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1.23.2: Water: Molar Volume

The molar volume $V_1^*(\ell)$ and density $\rho_1^*(\ell)$ of water(ℓ) are intensive properties. The $p - V - T$ properties of water are perhaps the most extensively studied. Two properties are almost universally known;

i. the molar volume of water at ambient pressure and $273.15\ K$ is less than that of ice, and
ii. the molar volume of water at $273.15\ K$ decreases on heating to reach a TMD before increasing.

At ambient pressure the temperature of maximum density for water, $TMD = 3.98\ Celsius$; for D_2O, $TMD = 11.44\ Celsius$. The TMD for SiO_2 is around 15270 Celsius, the dependence of density on temperature being less marked about the TMD than that for water [1].

The dependence of $V^*\ (H_2O; \ell)$ on temperature and pressure is reported by many laboratories. Most accounts cite the study reported by Kell and Whalley in 1965, later extended in 1978 [2,3]. Kell has examined the results in detail [4]. The TMD has, of course, attracted considerable attention. Nevertheless the TMD has no deep significance in the context of understanding the properties of water(ℓ). Other properties of water(ℓ) show extrema at other temperatures; e.g. isothermal compressibility near $300\ K$ [5-7].

Footnotes

[1] C. A. Angell and H. Kanno, Science, 1976,**193**,1121.

[2] G. S. Kell and E. Whalley, Philos. Trans. R. Soc. London, 1965,**258**,565.

[3] G. S. Kell, G. M. McLaurin and E.Whalley, Proc. R. Soc. London, Ser. A,1978,**360**,389.

[4] G. S. Kell, J. Chem. Eng. Data, 1967,12,66; 1975,20,97; 1970,**15**,119.

[5] R.A. Fine and F. J. Millero, J.Chem.Phys.,1975,63,89; 1973,**59**,5529.

[6] D.-P. Wang and F. J. Millero, J.Geophys. Res., 1973,**78**,7122.

[7] F. J. Millero, R. W. Curry and W. Drost-Hansen, J. Chem. Eng. Data, 1969, **14**,422.

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1.23.3: Water: Hydrogen Ions

Chemists are often faced with the situation where on adding salt MX to water(ℓ) experimental evidence shows that the cation exists as a hydrate $M(H_2O)_n$. For example, adding $CuSO_4(s)$, a white powder, to water produces a blue solution containing $[Cu(H_2O)_4]^{2+}$. If solute molecules bind solvent molecules to produce new solute molecules, one can imagine a limiting situation where, as the depletion of solvent continues, there is little 'solvent' as such left in the system.

An important example of the problems linked to description concerns hydrogen ions in aqueous solution [1]. Two common descriptions are

a. $H^+(aq)$, and
b. $H_3O^+(aq)$.

As a starting point, we assume that the system comprises n_j moles of solute HX and n_1 moles of water

A simple description of hydrogen ions is in terms of $H^+(aq)$ although intuitively the idea of protons as ions in aqueous solutions is not attractive. Arguably a more satisfactory description of hydrogen ions in solution is in terms of H_3O^+ ions. Description of hydrogen ions in aqueous solution as H_3O^+ finds general support. Adam recalls [2] the experiment conducted by Bagster and Cooling [3]. The latter authors observed that the electrical conductivity of a solution of HCl in $SO_2(\ell)$ is low but increases dramatically when 1 mole of water(ℓ) is added for each mole of HCl. Moreover on electrolysis, hydrogen ions and water are liberated at the cathode; water(ℓ) drips from this electrode.

In the chemistry of aqueous solutions, two ions H^+ and OH^- command interest. Hydrogen ions are also called [1] hydronium ions when written as H_3O^+. The latter ion is a flat pyramid with $d(O-H) = 96.3\ pm$; the HOH angle = 110-1120 [4]. A case for writing the formula H_3O^+ is based on the existence of isomorphous solids, $+ - NH_4^+ClO_4^-$ and $H_3O^+ClO_4^-$. The mass spectra of $H^+(H_2O)_n$ have been observed for $1 \legn \leq 8$ [5]. Neutron-scattering and X-ray scattering data show that for D_3O^+ ions in solution , $d(O-D) = 101.7\ pm$ [6]. In an 'isolated' H_3O^+ ion the $O-H$ bond length is $97\ pm$ and the HOH angle is 110 - 112.

In aqueous solution, H_3O^+ ions do not exist as solutes comparable to Na^+ ions in $NaCl(aq)$. Instead a given H_3O^+ ion transfers a proton to a neighboring water molecule. The time taken for the transfer is very short, approx. 10-13 seconds granted that the receiving water molecule has the correct orientation. But a given H_3O^+ ion has a finite lifetime, sufficient to be characterized by thermodynamic and spectroscopic properties The rate determining step in proton migration involves reorientation of neighboring water molecules, thereby accounting for the increase in molar conductance Extra \left or missing \right with increase in T and p [7 - 10]. [In ice, proton transfer is rate determining and so the mobilities of H^+ and OH^- ions are higher in ice than in water(ℓ).} The high mobility of protons in aqueous solution involves a series of isomerizations between $H_9O_4^+$ and $H_5\mahtrm{O}_2^+$, the first triggered by hydrogen bond cleavage of a second shell water molecule and the second by the reverse, hydrogen bond formation [11]. An iconoclastic approach, expressed by Hertz and co-workers, argues against the existence of H^+ ions as such except in so far as this symbol describes as dynamical property of a solution [12,13]. In their view H_3O^+ is ephemeral. Among other interesting ions discussed in this context are $H_5O_2^+$ [14].

Comparisons are often drawn between $NH_4^+(aq)$ and $H_3O^+(aq)$ ions but they are not really related. For example the electrical mobility of $NH_4^+(aq)$ is not exceptional.

The chemical potential of $H^+(aq)$ describes the change in Gibbs energy when $\delta n(H^+)$ moles are added at constant $n(H_2O)$, $n(X^-)$, T and p. The chemical potential of $H^+(aq)$ is related to the molality $m(H^+)\,[= n(H^+)/n_1 M_1]$ and the single activity coefficient $\gamma(H^+)$.

The Gibbs energy of an aqueous solution $G(aq)$ prepared using n_1 moles of water and n_j moles of acid $H^+\ X^-$ is given by the equation (a) (for the solution at defined T and p, which we assume is close to the standard pressure p^0).

$$G(aq) = n_1\,\mu_1(H_2O;aq) + n(H^+)\,\mu(H^+;aq) + n(X^-)\,\mu(X^-;aq)$$

where

$$\mu(H^+) = [\partial G/\partial n(H^+)]_{n(H_2O),n(X^-)}$$

and

$$\mu\left(H^{+};aq\right)=\mu^{0}\left(H^{+};aq\right)+R\,T\,\ln\left[m\left(H^{+}\right)\,\gamma\left(H^{+}\right)/m^{0}\right]$$

For the electrolyte $H^{+}\ X^{-}$ with $\nu=2$,

$$\mu\left(H^{+}X^{-};aq\right)=\mu^{0}\left(H^{+}X^{-};aq\right)+2\,R\,T\,\ln\left[m\left(H^{+}X^{-}\right)\,\gamma_{\pm}\left(H^{+}X^{-}\right)/m^{0}\right]$$

and, all T and p,

$$\text{limit}\left[m\left(H^{+}X^{-}\right)\rightarrow 0\right]\gamma_{\pm}=1.0$$

In a similar fashion, we define the partial molar volume, enthalpy and isobaric heat capacity for H^{+} in aqueous solution.

$$V\left(H^{+};aq;T;p\right)=\left[\partial V/\partial n\left(H^{+}\right)\right]_{T,p,n(H_{2}O),n(X^{-})}$$

$$H\left(H^{+};aq;T;p\right)=\left[\partial H/\partial n\left(H^{+}\right)\right]_{T,p,n(H_{2}O),n(X^{-})}$$

For electrolyte $H^{+}\ X^{-}$,

$$V^{\infty}\left(H^{+}X^{-};aq;T;p\right)=V^{\infty}\left(H^{+};aq;T;p\right)+V^{\infty}\left(X^{-};aq;T;p\right)$$

$$H^{\infty}\left(H^{+}X;aq;T;p\right)=H^{\infty}\left(H^{+};aq;T;p\right)+H^{\infty}\left(X^{-};aq;T;p\right)$$

and

$$C_{p}^{\infty}\left(H^{+}X^{-};aq;T;p\right)=C_{p}^{\infty}\left(H^{+};aq;T;p\right)+C_{p}^{\infty}\left(X^{-};aq;T;p\right)$$

The chemical potential of $H_{3}O^{+}$ ions in aqueous solution describes the change in Gibbs energy when $\delta n\left(H_{3}O^{+}\right)$ ions are added at constant $n\left(H_{2}O\right),\ n\left(X^{-}\right)$, T and p. At defined T and p,

$$\mu\left(H_{3}O^{+};aq\right)=\left[\partial G/\partial n\left(H_{3}O^{+}\right)\right]_{n(H_{2}O);n(X^{-})}$$

The chemical potential of the electrolyte $H_{3}O^{+}X^{-}$ in aqueous solution is described by the following equation.

$$\begin{aligned}&\mu\left(H_{3}O^{+}X^{-};aq\right)\\&=\mu^{0}\left(H_{3}O^{+}X^{-};aq\right)+2\,R\,T\,\ln\left[m\left(H_{3}O^{+}X^{-}\right)\,\gamma_{\pm}\left(H_{3}O^{+}X^{-}\right)/m^{0}\right]\end{aligned}$$

where

$$m\left(H_{3}O^{+}X^{-}\right)=n\left(H_{3}O^{+}X^{-}\right)/n\left(H_{2}0\right)\,M_{1}$$

$$n\left(H_{2}O\right)=n_{1}-n\left(H_{3}0^{+}\right)$$

and where

$$\text{limit}\left[m\left(H_{3}O^{+}X^{-}\right)\rightarrow 0\right)\gamma_{\pm}\left(H_{3}O^{+}X^{-}\right)=1.0\text{ at all T and p}$$

Thus the chemical potential $\mu\left(H_{3}O^{+}\ X^{-};aq;T;p\right)$ of the electrolyte $H_{3}O^{+}\ X^{-}$ is related to the molality $m\left(H_{3}O^{+}\ X^{-}\right)$ and the mean ionic activity coefficient $\gamma_{\pm}\left(H_{3}O^{+}\ X^{-}\right)$. We compare two descriptions of the same system. In description I, the system is an aqueous solution containing H^{+} and X^{-} ions whereas in description II the system is an aqueous solution containing $H_{3}O^{+}$ and X^{-} ions.

Description I; n_{j} moles of $H^{+}\ X^{-}$;

$$G(aq;I)=n_{1}\,\mu_{1}(aq;I)+n_{j}\,\mu\left(H^{+};aq;I\right)+n_{j}\,\mu\left(X^{-};aq;I\right)$$

Description II

$$G(aq;II)=\left(n_{1}-n_{j}\right)\,\mu_{1}(aq;II)+n_{j}\,\mu\left(H_{3}O^{+};aq\right)+n_{j}\,\mu\left(X^{-};aq;II\right)$$

At equilibrium,

a. $$G(I;aq)=G(II;aq)$$

b. $$\mu_{1}(aq;I)=\mu_{1}(aq;II)$$

c. $$\mu\left(\mathrm{X}^{-};\mathrm{aq};\mathrm{I}\right)=\mu\left(\mathrm{X}^{-};\mathrm{aq};\mathrm{II}\right)$$

At equilibrium (at defined T and p)

$$\mu\left(\mathrm{H}^{+};\mathrm{aq}\right)+\mu_1(\mathrm{aq})=\mu\left(\mathrm{H_3O}^{+};\mathrm{aq}\right)$$

In effect we shifted a mole of water for each mole of H^{+} ions from consideration as part of the solvent in description I to part of the solute in description II forming $\mathrm{H_3O}^{+}$ ions. The link between these descriptions is achieved through two formulations of $\mathrm{G}^{\mathrm{eq}}(\mathrm{aq})$ which is identical for both systems (as are V^{eq}, S^{eq} and H^{eq}). The equality of the total Gibbs function and equilibrium chemical potentials of substances common to both descriptions leads to equation (u) relating $\mu\left(\mathrm{H}^{+};\mathrm{aq}\right)$ and $\mu\left(\mathrm{H_3O}^{+};\mathrm{aq}\right)$. We take the analysis a stage further and use the equations relating chemical potential and composition for the two ions H^{+} and $\mathrm{H_3O}^{+}$ in aqueous solution at defined T and p.

Description I

$$\mathrm{m}\left(\mathrm{H}^{+}\right)=\mathrm{n}\left(\mathrm{H}^{+}\right)/\mathrm{n}_1\,\mathrm{M}_1 \qquad \mathrm{m}\left(\mathrm{X}^{-};\mathrm{I}\right)=\mathrm{n}\left(\mathrm{X}^{-}\right)/\mathrm{n}_1\,\mathrm{M}_1$$

Description II

$$\mathrm{m}\left(\mathrm{H_3O}^{+}\right)=\mathrm{n}\left(\mathrm{H_30}^{+}\right)/\left(\mathrm{n}_1-\mathrm{n}_\mathrm{j}\right)\,\mathrm{M}_1$$

and

$$\mathrm{m}\left(\mathrm{X}^{-};\mathrm{II}\right)=\mathrm{n}\left(\mathrm{X}^{-}\right)/\left(\mathrm{n}_1-\mathrm{n}_\mathrm{j}\right)\,\mathrm{M}_1$$

Also,

$$\mu^{eq}\left(\mathrm{H_3O}^{+};\mathrm{aq}\right)=\mu^{eq}\left(\mathrm{H}^{+};\mathrm{aq}\right)+\mu_1^{\mathrm{eq}}(\mathrm{aq})$$

Hence,

$$\begin{aligned}\mu^0\left(\mathrm{H_3O}^{+}\mathrm{X};\mathrm{aq}\right)+2\,\mathrm{R}\,\mathrm{T}\,\ln\left[\mathrm{m}\left(\mathrm{H_3O}^{+}\mathrm{X}\right)\,\gamma_\pm\left(\mathrm{H_3O}^{+}\mathrm{X}^{-}\right)/\mathrm{m}^0\right]\\ =\mu^0\left(\mathrm{H}^{+}\mathrm{X};\mathrm{aq}\right)+2\,\mathrm{R}\,\mathrm{T}\,\ln\left[\mathrm{m}\left(\mathrm{H}^{+}\mathrm{X}^{-}\right)\,\gamma_\pm\left(\mathrm{H}^{+}\mathrm{X}\right)/\mathrm{m}^0\right]\\ +\mu_1^*(\ell;\mathrm{T};\mathrm{p})-2\,\phi(\mathrm{I})\,\mathrm{R}\,\mathrm{T}\,\mathrm{m}^*\mathrm{H}^{+}\mathrm{X}^{\circ})\,\mathrm{M}_1\end{aligned}$$

But

$$\begin{aligned}&\mathrm{limit}\left(\mathrm{n}_\mathrm{j}\to 0\right)\mathrm{m}\left(\mathrm{H}^{+}\mathrm{X}^{-}\right)/\mathrm{m}\left(\mathrm{H_3O}^{+}\right)=1.0\\ &\gamma_\pm\left(\mathrm{H}^{+}\mathrm{X}^{-}\right)/\gamma_\pm\left(\mathrm{H_3O}^{+}\mathrm{X}^{-}\right)=1 \quad \phi(\mathrm{I})=1.0\end{aligned}$$

Hence,

$$\mu''\left(\mathrm{H_3O}^{+};\mathrm{aq}\right)=\mu''\left(\mathrm{H}^{+};\mathrm{aq}\right)+\mu_1^*\left(\mathrm{H_2O};\ell\right)$$

Also,

$$\mathrm{V}^{\infty}\left(\mathrm{H_3O}^{+};\mathrm{aq}\right)=\mathrm{V}^{\infty}\left(\mathrm{H}^{+};\mathrm{aq}\right)+\mathrm{V}_1^*\left(\mathrm{H_2O};\ell\right)$$

And

$$\mathrm{C}_\mathrm{p}^{\infty}\left(\mathrm{H_3O}^{+};\mathrm{aq}\right)=\mathrm{C}_\mathrm{p}^{\infty}\left(\mathrm{H}^{+};\mathrm{aq}\right)+\mathrm{C}_{\mathrm{pl}}^*\left(\mathrm{H_2O};\ell\right)$$

Interestingly the difference in reference chemical potentials of $\mathrm{H}^{+}(\mathrm{aq})$ and $\mathrm{H_3O}^{+}(\mathrm{aq})$ equals the chemical potential of water(ℓ) at the same T and p. We combine equations (z) and (za) to obtain an equation relating the mean ionic activity coefficients $\gamma_\pm\left(\mathrm{H}^{+}\mathrm{X}^{-}\right)$ and $\gamma_\pm\left(\mathrm{H_3O}^{+}\mathrm{X}^{-}\right)$. Thus (at defined T and p)

$$\begin{aligned}\ln\left[\gamma_\pm\left(\mathrm{H_3O}^{+}\mathrm{X}^{-}\right)\right]=\ln\left[\gamma_\pm\left(\mathrm{H}^{+}\mathrm{X}^{-}\right)\right]+\ln\left[\mathrm{m}\left(\mathrm{H}^{+}\mathrm{X}^{-}\right)/\mathrm{m}\left(\mathrm{H_3O}^{+}\mathrm{X}^{-}\right)\right]\\ -\phi(\mathrm{I})\,\mathrm{m}\left(\mathrm{H}^{+}\mathrm{X}^{-}\right)\,\mathrm{M}_1\\ +[1/2\,\mathrm{R}\,\mathrm{T}]\,\left[\mu^0\left(\mathrm{H}^{+}\mathrm{X}^{-};\mathrm{aq}\right)+\mu_1^*(\ell)-\mu^0\left(\mathrm{H_3O}^{+}\mathrm{X}^{-};\mathrm{aq}\right)\right]\end{aligned}$$

Then

$$\ln\left[\gamma_{\pm}\left(H_3O^+X^-\right)\right] = \ln\left[\gamma_{\pm}\left(H^+X^-\right)\right] + \ln\left[m\left(H^+X^-\right)/m\left(H_3O^+X^-\right)\right] - \phi(I)\, m\left(H^+X^-\right)\, M_1$$

Also from equations (v) and (w),

$$\ln\left[m\left(H^+X^-\right)/m\left(H_3O^+X^-\right) = \ln\left[1 - M_1\, m\left(H^+X^-\right)\right]\right.$$

Clearly in dilute aqueous solutions where $\{m\left(H^+X^-\right)/m\left(H_3O^+X-\right)\}$ is approximately unity and $\phi(I)\, m\left(H^+X^-\right)\, M_1$ is negligibly small, the two mean ionic activity coefficients are equal but this approximation becomes less acceptable with increase in the ratio $n\left(H^+X^-\right)/n\left(H_2O\right)$.

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1.23.4: Water: Relative Permittivity

Parallel with interest in the $\mathrm{p}-\mathrm{V}-\mathrm{T}$ properties of water(ℓ), enormous interest has been shown in the relative permittivity of water(ℓ) as a function of T and p. Owen and Brinkley [1] showed that a type of Tait equation could be used to express the $\mathrm{T}-\mathrm{p}$ dependence of the relative permittivity of many liquids, including water(l). In 1980, Uematsu and Franck reviewed published information concerning the permittivity of water(ℓ) and steam published over a period of 100 years [2,3].

A careful determination was reported by Deul in 1984 [4]. At $298.15\ \mathrm{K}$ and ambient pressure, the relative permittivities of water(ℓ) and $\mathrm{D_2O}(\ell)$ are 78.39 and 78.06 respectively [5]. A report by Owen and co-workers in 1961 stated a value of 78.358 for water(ℓ) at $298.15\ \mathrm{K}$. Bradley and Pitzer [7] survey published relative permittivities of water(ℓ) over an extensive temperature range.

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1.23.5: Water: Self-Dissociation

A significant contribution to the chemistry of aqueous solutions stems from the self dissociation of water(ℓ)(see also $D_2O(\ell)$ [1]). At $298.15\ K$ and ambient pressure, $pK_a equals 14.004 [2]. Olofsson and Hepler [3] recommended a `best value' for the standard enthalpy of self dissociation at ambient pressure and \(298.15\ K$ equal to $55.81\ kJmol^{-1}$ [4,5]. Hepler and colleagues recommend a best value for $\Delta_d C_p^0$ equal to $-215\ JK^{-1}\ mol^{-1}$ [5]; see also [6-8] together with [1] for details characterizing D_2O.

The standard volume of self-dissociation for water(ℓ) at $298\ K$ is negative, approx. $-20 cm^3\ mol^{-1}$, decreasing with increase in temperature [8,9].

An extensive literature describes the thermodynamics of self-dissociation of water in binary liquid mixtures [11]; see also [12] for D_2O.

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1.23.6: Water: (Shear) Viscosity

When the properties of water(ℓ) are reviewed, general practice is to identify the importance of intermolecular hydrogen bonding as a molecular cohesive force. In these terms it is perhaps a surprise to discover that water(ℓ) pours quite smoothly and freely, certainly more freely than, say, glycerol(ℓ). Indeed the viscosity of water(ℓ) is quite modest; $0.8903\ \mathrm{cP}$ at $298.15\ \mathrm{K}$ [1,2].

Nevertheless there are indications of complexity because below $230\ \mathrm{K}$ the viscosity of water(ℓ) decreases with increase in pressure before increasing. Good agreement exists between the results reported by many laboratories for viscosities of water(ℓ) at low pressures but disagreement at high pressure [3].

Footnotes

[1]

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1.14.1: Adiabatic

For a closed system undergoing a change in thermodynamic properties under the adiabatic constraint, heat does not cross between system and surroundings. The system is **thermally insulated** (i.e. adiabatically enclosed) from the surroundings. The First Law for closed systems has the following form.

$$\Delta \mathrm{U} = \mathrm{q} + \mathrm{w}$$

For changes under the adiabatic constraint, q is zero [1]. Then for adiabatic changes,

$$\Delta \mathrm{U} = \mathrm{w}.$$

Footnote

[1] ‘Adiabatic’ means impassable, from the Greek: ‘a = not’ + ‘dia = through’ + ‘bathos = deep’.

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1.14.2: Adsorption- Langmuir Adsorption Isotherm- One Adsorbate

The theoretical basis of Adsorption Isotherms is customarily described in terms of a balance of rates of adsorption and desorption. [1] Three important assumptions are made.

1. The adsorbate covers the surface up to complete coverage as a monolayer on the substrate (adsorbent).
2. There are no adsorbate-adsorbate interactions on the surface of the host substrate.
3. On the substrate all binding sites are equivalent. IUPAC recommends the use of variables expressed in terms of unit mass of adsorbent; $\mathrm{n}_j^{\mathrm{ad}}/\mathrm{w}$ is the specific reduced adsorption of chemical substance j where $\mathrm{n}_j^{\mathrm{ad}}$ is the amount of adsorbate bound to j mass w of adsorbent. In other words equations describing the process are transformed into intensive variables [2,3].

In many interesting cases, small molecules (guest, adsorbate) bind to larger polymeric molecules (host, adsorbent) which provide a surface on which the smaller (guest) molecules are adsorbed. Adsorption data for such systems often follow a Langmuir pattern. Here we use a thermodynamic approach in descriptions of a thermodynamic equilibrium. Most texts describing Langmuir adsorption use a `kinetic model', as indeed did Langmuir is his description of adsorption [1].

We consider the case where water is the solvent and substance j is the adsorbate. In the absence of adsorbate j, the surface of the adsorbent is covered with water. When adsorbate j is added to the system, the adsorption is described by the following equation.

$$\mathrm{j}\left(\mathrm{aq};\mathrm{x_j}\right)+\mathrm{H_2O}\left(\mathrm{ad};\mathrm{x_1^{ad}}\right)\rightarrow\mathrm{j}\left(\mathrm{ad};\mathrm{x_j^{ad}}\right)+\mathrm{H_2O}\left(\mathrm{aq};\mathrm{x_1}\right)$$

The latter equation describes a physical process rather than a 'chemical' reaction but the symbolism is common. Thus x_j is the mole fraction of solute j in the aqueous phase; $\mathrm{x_1^{ad}}$ is the mole fraction of water in a thin solution adjacent to the surface of the adsorbate; x_1 is the mole fraction of water in the aqueous solution.; $\mathrm{x_j^{ad}}$ is the mole fraction of the substance j in the adsorbed layer. The process represented by equation (a) involves displacement of water from the 'thin' solution next to the adsorbent into the bulk solution. The reverse process describes the displacement of substance j from this layer by water(λ). At equilibrium, the two driving forces are balanced. We use a simple on/off model for the adsorption in a closed aqueous system at fixed temperature T and fixed pressure p ($\cong p^0$).

$$\begin{array}{lllll}\text{Then,} & \mathrm{j(aq)} \Leftarrow & s\mathrm{j(ad)} & & \\ \text{At } \mathrm{t}=0, & \mathrm{n_j^0} & 0 & \mathrm{mol} & \\ \text{At } t=\infty & n_j^0-\xi & \xi & \mathrm{mol} & \end{array}$$

The latter condition refers to the equilibrium state; ξ is the extent of binding of guest solute j to the host adsorbate. To describe this equilibrium we need equations for the chemical potentials of $j(\mathrm{aq})$ and $j(\mathrm{ad})$. The fraction of adsorbent surface covered by chemical substance j is defined as θ. If there are N sites on the adsorbate for adsorption, the amount of sites occupied equals $\mathrm{N}\,\theta$ and the amount of vacant sites equals $[\mathrm{N}\,(1-\theta)]$.

The aim of the analysis is a plot showing the degree of occupancy of the surface of the adsorbent θ as a function of the equilibrium composition of the system. If the experiment involves calorimetry, we require equations which describe the heat q associated with injection of a small aliquot of a solution containing the adsorbate into a solution containing the adsorbent.

The chemical potential of adsorbed chemical substance j, $\mu_j(\mathrm{ad})$ is related to θ using a general equation.

$$\mu_\mathrm{j}(\mathrm{ad})=\mu_\mathrm{j}^0(\mathrm{ad})+\mathrm{R\,T}\,\ln[\mathrm{f}(\theta)]$$

In order to make progress we need an explicit equation for $\mathrm{f}(\theta)$; $\mu_\mathrm{j}^0(\mathrm{ad})$ is the chemical potential of an ideal adsorbate on an ideal adsorbent where $\theta=1/2$ at the same T and p [4]. At equilibrium the chemical potential of solute j in solution equals the chemical potential of the adsorbate. We express the composition of the solution in terms of the concentration of chemical substance j, c_j.

$$\text{At equilibrium.}\quad \mu_\mathrm{j}(\mathrm{aq})=\mu_\mathrm{j}(\mathrm{ad})$$

$$\text{For solute, j(aq)},\quad \mu_\mathrm{j}(\mathrm{aq})=\mu_\mathrm{j}^0(\mathrm{aq})+\mathrm{R\,T}\,\ln\left[\mathrm{c_j(aq)}\,\mathrm{y_j(aq)}/\mathrm{c_r}\right]$$

By definition, $\mathrm{c_r}=1\ \mathrm{moldm^{-3}}$; γ_j is the solute activity coefficient where,

$$\lim it\,(c_j\rightarrow 0)\,y_j(aq)=1\qquad \text{at all } T \text{ and } p$$

$\mu_j^0(\mathrm{aq})$ is the chemical potential of solute j in solution having unit concentration $\mathrm{c_j}$, the thermodynamic properties of solute j being ideal. From equations (c) and (e) the equilibrium condition (d) requires, by definition, that

\[\begin{aligned}
&\Delta_{\mathrm{ad}} \mathrm{G}^{0}=\mu_{\mathrm{j}}^{0}(\mathrm{ad})-\mu_{\mathrm{j}}^{0}(\mathrm{aq}) \\
&=-\mathrm{R} \, \mathrm{T} \, \ln [\mathrm{f}(\theta)]+\mathrm{R} \, \mathrm{T} \, \ln \left[\mathrm{c}_{\mathrm{j}}(\mathrm{aq}) \, \mathrm{y}_{\mathrm{j}}(\mathrm{aq}) / \mathrm{c}_{\mathrm{r}}\right] \\
&=-\mathrm{R} \, \mathrm{T} \, \ln \left(\mathrm{K}_{\mathrm{ad}}\right)
\end{aligned} \nonumber \]

The dimensionless property \(\mathrm{K}_{\mathrm{ad}}\) is the equilibrium adsorption constant which depends on both T and p [5].

$$\text{Then, } \mathrm{K_{ad}} = \mathrm{f}(\theta)\, \mathrm{c_r}/\mathrm{c_j}(\mathrm{aq})\, \mathrm{y_j}(\mathrm{aq})$$

We envisage a solution volume V prepared using $n_j{}^0$ moles of chemical substance j. [The assumption is usually made that the volume of the system is the volume of the solution.] The equilibrium concentration of substance j, $\mathrm{c_j^{eq}}(\mathrm{aq})$ is given by equation (i) where \(\xi^{\mathrm{eq}}\) is the equilibrium extent of adsorption

$$\mathrm{c_j^{eq}}(\mathrm{aq}) = \left(\mathrm{n_j^0} - \xi^{\mathrm{eq}}\right)/\mathrm{V}$$

$$\mathrm{K_{ad}} = \left[\mathrm{f}(\theta)/\left(\mathrm{n_j^0} - \xi\right)\right]\, \left[\mathrm{V}\, \mathrm{c_r}/\mathrm{y_j}(\mathrm{aq})\right]$$

Equation (j) describes the composition of the system. Granted therefore the applicability of equation (i) we anticipate specific applications of this equation will, at minimum, yield two pieces of information.

(i) Dependence of θ on total concentration of j in the system, $\mathrm{n_j^0/V}$.

(ii) Dependence of percentage of chemical substance j bound on total concentration of j in the system, n_j^0/V.

If the system is prepared using n_1 moles of water, the enthalpy of the system is given by equation (k).

$$\mathrm{H(\ system\ )} = \mathrm{n_1\, H_1(aq)} + \left(\mathrm{n_j^0} - \xi^{\mathrm{eq}}\right)\, \mathrm{H_j(aq)} + \xi^{\mathrm{eq}}\, \mathrm{H_j(ad)}$$

The dependence of enthalpy on the extent of adsorption is given by equation (λ).

$$\begin{aligned}
&[\partial \mathrm{H(\ system\ )}/\partial\xi\xi] = \\
&\mathrm{n_1}\ [\partial \mathrm{H_1(aq)}/\partial\xi] + \left(\mathrm{n_j^0} - \xi^{\mathrm{eq}}\right)\ [\partial \mathrm{H_j(aq)}/\partial\xi] - \mathrm{H_j(aq)} \\
&\qquad\qquad + \mathrm{H_j(ad)} + \xi^{\mathrm{eq}}\ [\partial \mathrm{H_j(ad)}/\partial\xi]
\end{aligned}$$

As a working hypothesis we assume that the properties of substance j are ideal both in solution and as adsorbate. In other words there are no solute $j \rightleftarrows$ solute j interactions in the aqueous solution, no bound $j \rightleftarrows$ bound j interactions between adsorbed molecules and no solute $j \rightleftarrows$ bound j interactions.

In summary the adsorbed j molecules form monolayers and the adsorbed molecules are non-interacting with other adsorbed j molecules and with j molecules in solution [6].

a. $\mathrm{y_j(aq)} = 1.0$
b. $[\partial \mathrm{H_1(aq)}/\partial\xi] = 0.0$
c. $[\partial \mathrm{H_j(aq)}/\partial\xi] = 0.0$
d. $[\partial \mathrm{H_j(ad)}/\partial\xi] = 0.0$

$$\text{Therefore, } [\partial \mathrm{H(\ system\ )}/\partial\xi\xi] = \mathrm{H_j(ad)}^0 - \mathrm{H_j(aq)}^\infty = \Delta_{\mathrm{ad}}\mathrm{H}^0$$

Here $\mathrm{H_j(aq)}^\infty$ is the limiting partial molar enthalpy of solute j meaning that in effect the solute molecules in solution are infinitely apart. $\mathrm{H_j(ad)}^0$ is the standard partial molar enthalpy of the adsorbate, implying that on the surface of the host adsorbent the adsorbate molecules are infinitely far apart; i.e. there are no adsorbate-adsorbate interactions. $\Delta_{\mathrm{ad}}\mathrm{H}^0$ is the standard molar enthalpy for the adsorption of substance j from aqueous solution on to the adsorbate.

In the next stage we require an equation for $\mathrm{f}(\theta)$ in order to obtain an explicit equation for the chemical potential of adsorbed substance j. We use the Langmuir model [4];

$$f(\theta) = \theta/(1-\theta)$$

θ is the fraction of the surface covered by the adsorbate at equilibrium, the fraction $(1-\theta)$ being left bare; note that θ is an intensive variable.

$$\text{Then } \mu_{\mathrm{j}}(\mathrm{ad}) = \mu_{\mathrm{j}}^{0}(\mathrm{ad}) + \mathrm{R\,T}\ \ln[\theta/(1-\theta)]$$

The standard state for adsorbed j molecules corresponds to the situation where $\theta = 1/2$; i.e $[\theta/(1-\theta)]$ is unity. It is interesting to put some numbers to these variables. We set $\chi = \ln[\theta/(1-\theta)]$. Then for $\theta = 0.1$, $\mathrm{R\,T}\,\chi = -2.197\,\mathrm{R\,T}$. Hence when the surface is less than 50% covered the chemical potential of the adsorbate is less than in the adsorbed standard state. For $\theta = 1/2$, $\mathrm{R\,T}\ \chi = 0$; at this stage the chemical potential of substance j in the adsorbed state equals that in the reference (standard) state. For $\theta = 0.9$, $\mathrm{R\,T}\ \chi = 2.197\,\mathrm{R\,T}$. As the surface occupancy passes 0.5, the chemical potential of the adsorbate increases above that in the reference state. According to equation (i) for a system where solute –j and adsorbate –j have ideal thermodynamic properties,

$$\mathrm{K_{ad}} = [\theta/(1-\theta)]\ \left[\mathrm{V\,c_r}/\left(\mathrm{n_j^0} - \xi\right)\right]$$

With increase in ξ so θ increases. Unfortunately we do not know how θ and ξ are related. One procedure assumes that θ is proportional to \(\xi_{\mathrm{eq}}\), the constant of proportionality being π [4].

$$\mathrm{K_{ad}} = [\pi\,\xi^{\mathrm{eq}}/\,(1-\pi\,\xi^{\mathrm{eq}})]\ \left[\mathrm{V\,c_r}/\left(\mathrm{n_j^0} - \xi^{\mathrm{eq}}\right)\right]$$

$$\text{Hence, } (\mathrm{K_{ad}/V})\ (1/\mathrm{c_r})\ \left(\mathrm{n_j^0} - \xi^{\mathrm{eq}}\right) = \pi\,\xi^{\mathrm{eq}}/\,(1-\pi\,\xi^{\mathrm{eq}})$$

By definition,$\beta = [\mathrm{K_{ad}/V\,c_r}]^{-1}$

$$\text{Then, } \pi\ (\xi^{\mathrm{eq}})^2 - \xi^{\mathrm{eq}}\ \left[1 + \pi\,\mathrm{n_j^0} + \beta\,\pi\right] + \mathrm{n_j^0} = 0$$

Equation (t) is a quadratic in the required variable \(\xi^{\mathrm{eq}}\). With increase in amount of solute j in the system so the extent of adsorption increases. Recognising that β is taken as a constant,

$$\left[\mathrm{d}\xi/\mathrm{dn_j^0}\right] = \left[1-\pi\,\xi^{\mathrm{eq}}\right]/\left[\beta\,\pi + \pi\ \left(\mathrm{n_j^0} - \xi^{\mathrm{eq}}\right) + \left(1-\pi\,\xi^{\mathrm{eq}}\right)\right]$$

Equation (u) leads to an estimate of the dependence of θ on the concentration of chemical substance j in the system. This analysis assumes no interactions between adsorbed molecules on the adsorbent. This assumption is probably too drastic. One approach which takes account of such interactions is the Freundlich Adsorption Isotherm [7]. The chemical potentials of the adsorbed chemical substance j is related to θ using equation (v).

$$\mu_{\mathrm{j}}(\mathrm{ad}) = \mu_{\mathrm{j}}^{0}(\mathrm{ad}) + \mathrm{R\,T}\ \ln[\theta/(1-\theta)] - \mathrm{R\,T\,a}\,\theta$$

The parameter 'a' is an adsorbate-adsorbate interaction parameter. For systems where $\mathrm{a} < 0$ (where θ is always positive) repulsion between adsorbed molecules raises the chemical potential above that described by the Langmuir model and disfavours adsorption. For system where $\mathrm{a} > 0$, attraction between adsorbed j molecules lowers their chemical potentials below the chemical potentials described by the Langmuir model; i.e. adsorption is enhanced above that required by the ideal model. But as for the Langmuir model, θ is dependent on the extent of adsorption and thus almost certainly on the geometric properties of guest and host.

If the thermodynamic properties of the solute j in solution are assumed to be ideal, equation (r) is rewritten as follows.

$$\mathrm{K_{ad}} = [\pi\,\xi^{\mathrm{eq}}/\,(1-\pi\,\xi^{\mathrm{eq}})]\ \exp\left(-\mathrm{a}\,\pi\,\xi^{\mathrm{eq}}\right)\ \left[\mathrm{V\,c_r}/\left(\mathrm{n_j^0} - \xi^{\mathrm{eq}}\right)\right]$$

Another approach writes $\mathrm{f}(\theta)$ using a general equation having the following form.

$$\mathrm{f}(\theta) = \left[\frac{\theta}{1-\theta}\right]\ \left[\frac{1}{\mathrm{n^n}}\right]\ \left[\frac{\theta + \mathrm{n}\,(1-\theta)}{1-\theta}\right]^{\mathrm{n}-1}$$

For the Langmuir adsorption isotherm, n is unity. Otherwise n is a positive integer; $\mathrm{n} = 1, 2, 3, \ldots$.Thus when n is set at 2 [5],

$$f(\theta) = \left[\frac{\theta}{1-\theta}\right]\ \left[\frac{1}{4}\right]\ \left[\frac{2-\theta}{1-\theta}\right]$$

We comment on terminology. In enzyme chemistry, the term **substrate** refers to (in relative terms) small molecules which bind to an enzyme, a macromolecule. However in the subject describing **adsorption** of molecules on a surface, the molecules which are

adsorbed are called the adsorbate. The macromolecular host is the **adsorbent** or **substrate**. In other words the meaning of the term '**substrate**' differs in the two subjects.

In general terms each enzyme has a unique site at which the adsorbate (substrate) is bound. However the term **adsorbent** implies that the 'surface' has a number of sites at which the adsorbate is adsorbed. The extent to which the sites are specific to a particular adsorbent is often less marked than in the case of enzymes. Nevertheless there is a common theme in which a substance j 'free' in solution loses translational freedom by coming in contact with a larger molecular system, being then held by that system.

Footnotes

[1] I. Langmuir, J.Am.Chem.Soc.,1918,**40**,1361.

[2] D. H. Everett, Pure Appl. Chem.,1986, **58**, 967.

[3] J. O'M. Bockris and S. U. M. Khan, Surface Electrochemistry, Plenum Press, New York, 1993.

[4] B. E. Conway, H. Angerstein-Kozlowska and H. P. Dhar, Electrochim.Acta, 1975, **19**,189.

[5] M. J. Blandamer, B. Briggs, P. M. Cullis, K. D. Irlam, J. B. F. N. Engberts and J. Kevelam, J. Chem. Soc. Faraday Trans.,1998, **94**,259.

[6] K. S. Pitzer, Thermodynamics, McGraw-Hill, New York, 3rd edn., 1995,chapter 23.

[7] H. Freundlich, Z.Phys.Chem.,1906,**57**,384.

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1.14.3: Absorption Isotherms - Two Absorbates

We consider the case where in addition to the adsorbent there are two adsorbates, chemical substances i and j in aqueous solution [1]. In the simplest case the thermodynamic properties of the system are ideal. In other words for both solutes and adsorbates there are no $i-i$, $j-j$ and $i-j$ interactions. Analysis of the adsorption using the Langmuir adsorption isotherm leads to two terms describing the surface coverage, θ_i and θ_j plus the total surface coverage, $\theta_i+\theta_j$. The chemical potentials of the solutes in solution are described in terms of their concentrations (assuming pressure p is close to the standard pressure); \mathrm{c}_{\mathrm{r}}=1 \mathrm{~mol dm}^{-3}.

$$\mu_j(aq) = \mu_j^0(aq) + RT\,\ln(c_j/c_r)$$

$$\mu_i(aq) = \mu_i^0(aq) + RT\,\ln(c_i/c_r)$$

The upper limit of the total surface occupancy is unity and so we expect as $(\theta_i+\theta_j)$ approaches unity the sum of the chemical potentials $\mu_j(\mathrm{ad})$ and $\mu_i(\mathrm{ad})$ approaches $+\infty$, thereby opposing any tendency for further solute to be adsorbed. If we assert that there are no substrate-substrate interactions on the surface, the chemical potential of adsorbate j can be formulated as follows.

$$\mu_j(\mathrm{ad}) = \mu_j^0(\mathrm{ad}) + \mathrm{R\,T\,ln}\left[\theta_\mathrm{j}/\left(1-\theta_\mathrm{i}-\theta_\mathrm{j}\right)\right]$$

The denominator $(1-\theta_i-\theta_j)$ takes account of the fact that adsorbate i also occupies the surface. Thus as $(\theta_i+\theta_j)$ approaches unity there are no more sites on the surface for adsorbate j (and adsorbate i) to occupy.

$$\text{Thus } \lim\left[(1-\theta_\mathrm{i}-\theta_\mathrm{j})\to 0\right]\mu_\mathrm{j}(\mathrm{ad}) = +\infty$$

The equilibrium between chemical substance j as solute and adsorbate is described as follows.

$$\text{Solute } -\mathrm{j}+ \text{ Polymer Surface } \Leftrightarrow \text{ Adsorbate j}$$

$$\text{Prepared } \mathrm{n_j^0} \qquad 0 \text{ mol}$$

$$\text{Equilib.} \quad \mathrm{n_j^0-\xi_j} \quad \xi_\mathrm{j}+\xi_\mathrm{i} \quad \xi_\mathrm{j}\mathrm{mol}$$

We express the fraction of surface coverage as proportional to the extent of adsorption via a proportionality constant π which is a function of the sizes of the solutes and geometric parameters describing the surface.

$$\text{Then,} \quad \theta_i = \pi_i\,\xi_i \quad \text{and } \theta_j = \pi_j\,\xi_j$$

$$\text{At equilibrium } \mu_\mathrm{j}^{\mathrm{eq}}(\mathrm{aq}) = \mu_\mathrm{j}^{\mathrm{eq}}(\mathrm{ad}) \text{ and } \mu_\mathrm{i}^{\mathrm{eq}}(\mathrm{aq}) = \mu_\mathrm{i}^{\mathrm{eq}}(\mathrm{ad})$$

Hence for a system having volume V,

$$\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R\,T\,ln}\left[\left(\mathrm{n_j^0}-\xi_\mathrm{j}\right)/\mathrm{V\,c_r}\right] = \mu_\mathrm{j}^0(\mathrm{ad}) + \mathrm{R\,T\,ln}\left[\frac{\pi_\mathrm{j}\,\xi_\mathrm{j}}{1-\pi_\mathrm{j}\,\xi_\mathrm{j}-\pi_\mathrm{i}\,\xi_\mathrm{i}}\right]$$

$$\text{By definition, } \Delta_{\mathrm{ad}}\mathrm{G_j^0} = -\mathrm{R\,T\,ln\,K_j} = \mu_\mathrm{j}^0(\mathrm{ad}) - \mu_\mathrm{j}^0(\mathrm{aq})$$

$$\text{Hence, } \mathrm{K_j} = \left[\frac{\pi_\mathrm{j}\,\xi_\mathrm{j}}{1-\pi_\mathrm{j}\,\xi_\mathrm{j}-\pi_\mathrm{i}\,\xi_\mathrm{i}}\right]\frac{\mathrm{V\,c_r}}{\left(\mathrm{n_j^0}-\xi_\mathrm{j}\right)}$$

A similar equation is obtained for equilibrium constant K_i. Both equations are quadratics in the extent of adsorption

Footnotes

[1] M. J. Blandamer, B. Briggs, P. M. Cullis, K. D. Irlam, J. B. F. N. Engberts and J. Kevelam, J. Chem. Soc. Faraday Trans.,1998, **94**, 259.

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1.14.4: Apparent Molar Properties- Solutions- Background

A given solution, volume V, is prepared using n_1 moles of solvent (e.g. water) and n_j moles of solute, chemical substance j.

Thus

$$V(aq) = n_1\,V_1(aq) + n_j\,V_j(aq) \tag{1.14.4.1}$$

Here $\mathrm{V}_1(\mathrm{aq})$ is the partial molar volume of the solvent and $\mathrm{V}_j(\mathrm{aq})$ is the partial molar volume of the solute-j [1]. Experiment yields the density of this solution at defined T and p. In order to say something about this solution we would like to comment on the two partial molar volumes, $\mathrm{V}_1(\mathrm{aq})$ and $\mathrm{V}_2(\mathrm{aq})$. But we have only three known variables; the amounts of solvent and solute and the density. If we change the amount of, say, solute then $\mathrm{V}(\mathrm{aq})$ together with the two partial molar volumes change. So we end up with more unknowns than known variables. Hence it would appear that no progress can be made. All is not lost. Equation (a) is rewritten in terms of the molar volume of the solvent, $\mathrm{V}_1^*(\lambda)$ which is calculated from the density of the pure solvent and its molar mass. At a given T and p, density $\rho_1^*(\lambda) = \mathrm{M}_1/\mathrm{V}_1^*(\lambda)$. We replace $\mathrm{V}_j(\mathrm{aq})$ in Equation 1.14.4.1 by the apparent molar volume, $\phi\,(\mathrm{V}_j)$; Equation 1.14.4.2.

$$\mathrm{V(aq)} = \mathrm{n}_1\,\mathrm{V}_1^*(\lambda) + \mathrm{n_j}\,\phi\,(\mathrm{V_j}) \tag{1.14.4.2}$$

Now we have only one unknown variable. But we anticipate that the apparent molar volume $\phi\,(\mathrm{V}_j)$ depends on the composition of the solution, the solute, T and p.

These comments concerning partial molar volumes establish a pattern which can be carried over to other partial molar properties. The following apparent molar properties of solutes are important; (i) apparent molar enthalpies $\phi\,(\mathrm{H_j})$, (ii) apparent molar isobaric heat capacities $\phi\,(\mathrm{C}_{pj})$, (iii) apparent molar isothermal compressions $\phi\,(\mathrm{K_{T_j}})$, and (iv) apparent molar isobaric expansions $\phi\,(\mathrm{E_{pj}})$. Apparent molar (defined) isentropic compressions $\phi\,(K_{\mathrm{Sj}};\mathrm{def})$, and apparent molar (defined) isentropic expansions $\phi\,(K_{\mathrm{Sj}};\mathrm{def})$ are also quoted but new complexities emerge.

Lewis and Randall commented [2] that ‘apparent molal quantities have little thermodynamic utility’, a statement repeated in the second [3] but not in the third edition of this classic monograph.[4] Suffice to say, their utility in the analysis of experimental results has been demonstrated by many authors.

Apparent molar properties of solutes $\phi\,(\mathrm{E_{pj}})$, $\phi\,(K_{\mathrm{Sj}};\mathrm{def})$, $\phi\,(\mathrm{K_{T_j}})$, $\phi\,(K_{\mathrm{Sj}};\mathrm{def})$ and $\phi\,(\mathrm{C}_{pj})$ are calculated using in turn the extensive properties of solutions, isobaric expansions E_p, isentropic expansions $\mathrm{E_S}$, isothermal compressions $\mathrm{K_T}$, isentropic compressions $\mathrm{K_S}$ and isobaric heat capacities C_p.

Footnotes

[1] Equation (a) is interesting . We do not have to add the phrase ‘at constant temperature and pressure’

[2] G. N. Lewis and M. Randall, Thermodynamics and The Free Energy of Chemical Substances, McGraw-Hill, New York, 1923. [The title on the front cover of the monograph is simply ‘Thermodynamics’.]

[3] G. N. Lewis and M. Randall, Thermodynamics, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 2nd. edn. 1961, p. 108.

[4] K. S. Pitzer, Thermodynamics, McGraw-Hill, New York, 3d. edn., 1995.

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1.14.5: Apparent Molar Properties- Solutions- General

Consider the general apparent molar property $\phi\,(\mathrm{Q}_j)$ and the corresponding extensive property of a solutions, Q; e.g. C_p, E_p, E_S, K_T and K_S. The latter are all extensive properties of a given system. The corresponding volume intensive property q is given by the ratio Q/V; c.f. q = isobaric expansivity α_p, isentropic expansivity α_S, isothermal compressibility K_T, isentropic compressibility K_S, and heat capacitance σ respectively. The following four general equations [1] show how the volume intensive properties of the solution and solvent, q and $q_1{}^*$ respectively, form the basis for the calculation of apparent molar property $\phi\,(Q_j)$ [2].

$$\phi\,(Q_j) = (q - q_1^*)\;(m_j\,\rho_1^*)^{-1} + q\,\phi\,(V_j)$$

$$\phi\,(Q_j) = (q - q_1^*)\;(c_j)^{-1} + q_1^*\,\phi\,(V_j)$$

$$\phi\,(Q_j) = (q\,\rho_1^* - q_1^*\,\rho)\;(m_j\,\rho\,\rho_1^*)^{-1} + q\,M_j\,\rho^{-1}$$

$$\phi\,(Q_j) = (q\,\rho_1^* - q_1^*\,\rho)\;(c_j\,\rho_1^*)^{-1} + q_1^*\,M_j\;(\rho_1^*)^{-1}$$

In these four equations, ρ is the density of the solution; $\rho_1{}^*$ is the density of the solvent at the same T and p. The theme running through these equations is the link between the apparent molar property $\phi\,(Q_j)$ of a given solute and the measured property q. Interestingly apparent molar enthalpies break the pattern in that the enthalpy of a solution cannot be measured. Nevertheless apparent molar enthalpies are used in the analysis of calorimetric results. There are no advantages in defining apparent chemical potentials and apparent molar entropies of solutes.

Footnotes

[1] M. J. Blandamer, M. I. Davis, G.Douheret and J. C. R. Reis, Chem. Soc. Rev.,2001, **30**,8.

[2] $\phi\,(Q_j)$ is defined by the following equation with reference to the extensive variable Q in terms of amounts of solvent and solute n_1 and n_j respectively where $\mathrm{Q}_1{}^*$ is the molar property of the solvent at the same T and p.

$$Q = n_1\,Q_1^* + n_j\,\phi\,(Q_j)$$

We shift to volume intensive properties q and $q_1{}^*$.

$$\mathrm{V\,q} = \mathrm{n_1\,V_1^*(\lambda)\,q_1^* + n_j\,\phi\,(Q_j)}$$

We express the volume using the following equation incorporating apparent molar volume $\phi\,(\mathrm{V_j})$ and molar volume of the solvent $V_1^*(\lambda)$ at the same T and p.

$$\mathrm{V = n_1\,V_1^*(\lambda) + n_j\,\phi\,(V_j)}$$

We solve equation (b) for $\phi\,(\mathrm{V_j})$ using equation (c).

$$\text{Hence, } \phi\,(\mathrm{Q_j}) = \frac{\mathrm{n_1\,V_1^*(\lambda)\,q}}{\mathrm{n_j}} + \mathrm{q}\,\phi\,(\mathrm{V_j}) - \frac{\mathrm{n_1\,V_1^*(\lambda)\,q_1^*}}{\mathrm{n_j}}$$

But [3] $\mathrm{n_1\;V_1^*(\lambda)/n_j = (m_j\,\rho_1^*)^{-1}}$.

Equation (e) follows.

$$\phi\,(Q_j) = (q - q_1^*)\;(m_j\,\rho_1^*)^{-1} + q\,\phi\,(V_j)$$

Using the latter equation, molalities are converted to concentrations using equation (f).

$$\mathrm{(m_j\,\rho_1^*)^{-1} = (c_j)^{-1} - \phi\,(V_j)}$$

$$\text{Then } \phi\,(Q_j) = (q - q_1^*)\;(c_j)^{-1} - \phi\,(V_j)\;(q - q_1^*) + q\,\phi\,(V_j)$$

$$\text{Or } \phi\,(Q_j) = (q - q_1^*)\;(c_j)^{-1} + q_1^*\,\phi\,(V_j)$$

We return to equation (b) and express the volume using the following equation.

$$\mathrm{V = [n_1\,M_1 + n_j\,M_j]\,/\rho}$$

$$\text{Then [4] } \phi\left(Q_j\right) = \frac{n_1\, M_1\, q}{n_j\, \rho} + \frac{M_j\, q}{\rho} - \frac{n_1\, V_1^*\, q_1^*}{n_j}$$

$$\text{Then [3,5] } \phi\left(Q_j\right) = \frac{q}{m_j\, \rho} + \frac{M_j\, q}{\rho} - \frac{q_1^*}{m_j\, \rho_1^*}$$

Or,

$$\phi\left(Q_j\right) = \\ \left(q\, \rho_1^* - q_1^*\, \rho\right)\, \left(m_j\, \rho\, \rho_1^*\right)^{-1} + q\, M_j\, \rho^{-1}$$

To obtain an equation using concentrations, we use the following equation. $1/\mathrm{m_j} = \rho/\mathrm{c_j} - \mathrm{M_j}$

Thus [6]

$$\phi\left(Q_j\right) = \frac{q\, \rho_1^* - q_1^*\, \rho}{c_j\, \rho_1^*} - \frac{M_j\, \left(q\, \rho_1^* - q_1^*\, \rho\right)}{\rho_1^*\, \rho} + \frac{q\, M_j}{\rho}$$

Or,

$$\phi\left(Q_j\right) = \left(q\, \rho_1^* - q_1^*\, \rho\right)\, \left(c_j\, \rho_1^*\right)^{-1} + q_1^*\, M_j\, \left(\rho_1^*\right)^{-1}$$

Because the equations used for converting molalities to concentrations are exact, no approximations are involved. Therefore equations (e), (h),(λ) and m) are rigorously equivalent.

[3]

$$\mathrm{n_1\, V_1^*(\lambda)/n_j} = \mathrm{n_1\, V_1^*(\lambda)\, \rho_1^*(\lambda)/n_j\, \rho_1^*(\lambda)} \\ = \mathrm{w_1/n_j\, \rho_1^*(\lambda) = [m_j\, \rho_1^*(\lambda)]^{-1}}$$

[4] From equations (b) and (i),

$$\left(\mathrm{n_1\, M_1 + n_j\, M_j}\right)\, \mathrm{q}/\rho = \mathrm{n_1\, V_1^*(\lambda)\, q_1^* + n_j\, \phi\left(Q_j\right)}$$

[5] $\mathrm{n_1\, M_l/n_j} = \left(\mathrm{m_j}\right)^{-1}$

[6] From equation (λ), $\phi\left(Q_j\right) = \left\{\left[q\, \rho_1^*(\lambda) - q_1^*\, \rho\right]/\rho\, \rho_1^*(\lambda)\right\}\, \left[\left(\rho/c_j\right) - M_j\right] + \left[q\, M_j/\rho\right]$

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1.14.6: Axioms

An axiom is a statement of principle which is generally accepted to be true. Axioms cannot be conveniently demonstrated otherwise there would be no need to use axioms. The Laws of Thermodynamics are axioms [1]. However we can test and confirm by experiment many of the consequences following from the Laws of Thermodynamics. We can debate (if we so wish) if these laws were actually discovered in the sense that the laws were always there. Alternatively we might argue that these laws were formulated by brilliant scientists because prior to their formulation these laws did not exist.

Footnote

[1] M. L. McGlashan, J.Chem.Educ.,1966,**43**,226.

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1.14.7: Boundary

The term ‘boundary’ is encountered in several contexts in thermodynamics. Indeed the definition becomes more complicated as we concentrate on the thermodynamic properties of systems.

As a starting point, a boundary separates system and surroundings. A boundary is an infinitely thin surface separating system and surroundings such that the properties of system and surroundings change abruptly at the boundary. [1,2] In these terms a reaction vessel is part of the surroundings. We support this careful distinction by observing that if chemical reaction inside the system is exothermic, the liberated heat warms the reaction vessel. In this case, the boundary encloses the system. No molecules can either enter or leave the system. However heat is allowed to cross the boundary. Thus the whole universe is divided into system and surroundings [3], the only role of the boundary is to facilitate communication between system and surroundings. In these terms chemical substances, heat, and electric charge may cross a boundary between a system and surroundings.

In some cases the container (e.g. reaction vessel) may be considered part of the system. In many cases [4,5] it is correct to do so and so the boundary is again a hypothetical surface separating ‘reaction solution + reaction vessel’ and the surroundings.

In general terms, it is important to define the boundary for a given system. Another term for boundary is ‘envelope’ which indicates something which can be quite dynamic in terms of shape and volume rather than, for example, a glass vessel. Moreover the boundary may be selectively permeable to one or more chemical substances rather like the envelope of unit cells in living systems [6].

The term ‘boundary’ in the context of surface chemistry means a boundary phase (or, capillary phase) [7]. In such a phase there is a concentration gradient of one or more chemical substances across the boundary phase between system and surroundings. Indeed surface chemistry can be described as the chemistry of boundaries.

In summary we repeat the point that in a thermodynamic analysis of experimental results, a first requirement is that the system, boundary and surroundings are carefully defined. For the most part we assume that the boundary is an infinitely thin envelope separating system and surroundings.

Footnotes

[1] K. S. Pitzer, Thermodynamics, McGraw-Hill, New York,1995, 3rd. edn., page 6.

[2] G. N. Lewis and M. Randall, Thermodynamics, McGraw-Hill, New York, 1923, page 10.

[3] D. H. Everett, Chemical Thermodynamics, Longmans, London, 1959, page 8.

[4] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979,page 1.

[5] E. B. Smith, Basic Chemical Thermodynamics, Clarendon Press, Oxford, 3rd. edn.,1982, page 2.

[6] S. E. Wood and R. Battino, Thermodynamics of Chemical Systems, Cambridge University Press, Cambridge, 1990, page 3.

[7] J. N. Bronsted, Physical Chemistry, Heinemann, London, 1937, page 359.

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1.14.8: Calculus

Consider a variable u defined by the independent variables x and y.

$$\text{We write } u = u[x, y]$$

Equation (b) is the general exact differential of equation (a).

$$\mathrm{du} = \left(\frac{\partial \mathrm{u}}{\partial \mathrm{x}}\right)_{\mathrm{y}} \mathrm{dx} + \left(\frac{\partial \mathrm{u}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \mathrm{dy}$$

In other words the change in u is related to the differential dependence of u on x at constant y and the differential dependence of u on y at constant x. For the case where u does not change,

$$\left(\frac{\partial u}{\partial x}\right)_y = -\left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_u = 0 \text{ and } \left(\frac{\partial y}{\partial x}\right)_u = -\left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial y}{\partial u}\right)_x$$

A variable z is defined by the independent variables x and y.

$$z = z[x, y]$$

Equation (e) is the general differential of equation (d). d z=\left(\frac{\partial z}{\partial x}\right)_{y} \, d x+\left(\frac{\partial z}{\partial y}\right)_{x} \, d y \nonumber \]

We direct attention to the dependence of z on x along a pathway for which u is constant.

$$\text{Then } \left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_u$$

The latter equation contains the differential dependence of y on x at constant u. The latter dependence can be reformulated using equation (c). Therefore

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y - \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial y}{\partial u}\right)_x \left(\frac{\partial z}{\partial y}\right)_x$$

The key point to emerge from this exercise centres is the way in which the condition on the partial differential $(\partial z/\partial x)$ can be changed from ‘at constant y’ to ‘at constant u’.

Another important operation concerns a variable q.

$$\text{Thus, } \left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial q}\right)_z \left(\frac{\partial q}{\partial y}\right)_z$$

For composite functions such as $z = z[\mathrm{u}, \mathrm{v}]$, where $z = z[x, y]$, and $\mathrm{u} = \mathrm{u}[\mathrm{x}, \mathrm{y}]$, further important equations are found [1].

$$\text{Thus } \left(\frac{\partial z}{\partial u}\right)_v = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_v$$

Equation (i) is an example of the well-known chain rule, a similar equation holding for $(\partial z/\partial v)_u$. This rule allows the total change of independent variables from $z = z[\mathrm{u}, \mathrm{v}]$ to $z = z[x, y]$.

$$\text{Also } \left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_{y,v} + \left(\frac{\partial z}{\partial v}\right)_{y,x} \left(\frac{\partial v}{\partial x}\right)_y$$

The latter equation is useful for introducing an extra constraint on a given differential.

Footnote

[1] H. B. Callen, Thermodynamics and an Introduction to Thermostatics, Wiley, New York, 2dn. Edn.,1985, Appendix A.

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1.14.9: Clausius - Clapeyron Equation

A give closed system contains chemical substance j present in both liquid and gas phases. The system is at equilibrium. In terms of the Phase Rule, the following parameters are defined; $\mathrm{P} = 2$, $\mathrm{C} = 1$ and hence $\mathrm{F} = 1$. Hence, if the temperature is fixed by the observer, the equilibrium pressure p^{eq} is defined. The equilibrium can be described in terms of an equality of chemical potentials of pure liquid and pure gas.

$$\mu_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p}) \tag{1.14.9.1}$$

Both chemical potentials in Equation 1.14.9.1 are functions of both T and p. In general terms,

$$\mathrm{d}\mu_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p}) = \left(\frac{\partial\mu_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})}{\partial\mathrm{T}}\right)_{\mathrm{p}}\mathrm{dT} + \left(\frac{\partial\mu_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})}{\partial\mathrm{p}}\right)_{\mathrm{T}}\mathrm{dp} \tag{1.14.9.2}$$

or

$$\mathrm{d}\mu_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p}) = -\mathrm{S}_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})\,\mathrm{dT} + \mathrm{V}_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})\,\mathrm{dp} \tag{1.14.9.3}$$

Similarly

$$\mathrm{d}\mu_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p}) = -\mathrm{S}_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p})\,\mathrm{dT} + \mathrm{V}_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p})\,\mathrm{dp} \tag{1.14.9.4}$$

The condition in Equation 1.14.9.1 applies at all T and p.

$$\begin{aligned}&\text{Then, } -\mathrm{S}_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})\,\mathrm{dT} + \mathrm{V}_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})\,\mathrm{dp}\\ &= -\mathrm{S}_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p})\,\mathrm{dT} + \mathrm{V}_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p})\,\mathrm{dp}\end{aligned}$$

or [1],

$$\left(\frac{\mathrm{dp}}{\mathrm{dT}}\right)^{eq} = \frac{\mathrm{S}_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p}) - \mathrm{S}_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})}{\mathrm{V}_{\mathrm{j}}^{*}(\mathrm{gp};\mathrm{T};\mathrm{p}) - \mathrm{V}_{\mathrm{j}}^{*}(\ell;\mathrm{T};\mathrm{p})}$$

$$\left(\frac{\mathrm{dp}}{\mathrm{dT}}\right)^{\mathrm{eq}} = \frac{\Delta_{\mathrm{vap}}\mathrm{S}_{\mathrm{j}}^{*}(\ \mathrm{T};\mathrm{p})}{\Delta_{\mathrm{vap}}\ \mathrm{V}_{\mathrm{j}}^{*}(\ \mathrm{T};\mathrm{p})}$$

But at equilibrium,

$$\Delta_{\mathrm{vap}}\ \mathrm{G}_{\mathrm{j}}^{*}(\ \mathrm{T};\mathrm{p}) = \Delta_{\mathrm{vap}}\ \mathrm{H}_{\mathrm{j}}^{*}(\ \mathrm{T};\mathrm{p}) - \mathrm{T}\,\Delta_{\mathrm{vap}}\ \mathrm{S}_{\mathrm{j}}^{*}(\ \mathrm{T};\mathrm{p}) = 0$$

$$\left(\frac{\mathrm{dp}}{\mathrm{dT}}\right)^{\mathrm{eq}} = \frac{\Delta_{\mathrm{vap}}\ \mathrm{H}_{\mathrm{j}}^{*}(\ \mathrm{T};\mathrm{p})}{\mathrm{T}\,\Delta_{\mathrm{vap}}\mathrm{V}_{\mathrm{j}}^{*}(\ \mathrm{T};\mathrm{p})}$$

The latter is the Clausius-Clapeyron Equation [2]. In a modern development, equation (i) was exactly integrated [3]. Equation(i) does not have the form of an exact differential in the independent variables p and T.[3] The corresponding integrating factor is T^{-1} $\Delta_{\mathrm{vap}}\ \mathrm{V}_{\mathrm{j}}^{*}$.

Thus

$$\mathrm{T}^{-1}\,\Delta_{\mathrm{vap}}\ \mathrm{V}_{\mathrm{j}}^{*}\,\mathrm{dp} - \mathrm{T}^{-2}\,\Delta_{\mathrm{vap}}\ \mathrm{H}_{\mathrm{j}}^{*}\,\mathrm{dT} = 0$$

or,

$$\mathrm{T}^{-1}\,\Delta_{\mathrm{vap}}\ \mathrm{V}_{\mathrm{j}}^{*}\,\mathrm{dp} + \Delta_{\mathrm{vap}}\ \mathrm{H}_{\mathrm{j}}^{*}\,\mathrm{dT}^{-1} = 0$$

The latter equation is an exact differential as a consequence of equation (ℓ) [4].

$$\left(\frac{\partial\left(\mathrm{T}^{-1}\,\Delta_{\mathrm{vap}}\ \mathrm{V}_{\mathrm{j}}^{*}\right)}{\partial\mathrm{T}^{-1}}\right)_{\mathrm{p}} = \left(\frac{\partial\Delta_{\mathrm{vap}}\mathrm{H}_{\mathrm{j}}^{*}}{\partial\mathrm{p}}\right)_{\mathrm{T}}$$

A mathematical solution is known for differential equations having the form of equation (k) [3]. A comprehensive set of equations have been derived describing first order transitions for pure substances [5] and hence the phase equilibrium curves For liquid-

vapour equilibria, both $\Delta_{vap}\,H_j^*(\,T;p)$ and $\Delta_{vap}\,V_j^*(\,T;p)$ are >0. Therefore the equilibrium vapor pressure of a liquid increases with increase in temperature. A useful approximation assumes that gas j is a perfect gas; i.e. $p\,V_j^*(gp) = R\,T$ and $V_j^*(gp;T;p) >> V_j^*(l;T;p)$.

$$\left(\frac{d\ln(p)}{dT}\right)^{eq} = \frac{\Delta_{vap}\,H_j^*(\,T;p)}{R\,T^2}$$

$$\left(\frac{d\ln(p)}{d\,(T^{-1})}\right)^{eq} = -\frac{\Delta_{vap}H_j^*(\,T;p)}{R}$$

Within the limits of the approximations outlined above, $\ln\,(p^{eq})$ is a linear function of T^{-1}.

Exactly integrated equations have also been established for other first-order transitions (peq, Teq) curves of pure substances [5].

Footnotes

[1] $\frac{[Nm^{-2}]}{[K]} = \frac{[Jmol^{-1}\,K^{-1}]}{[m^3\,mol^{-1}]} = \frac{[Jm^{-3}]}{[K]} = \frac{[Nm^{-2}]}{[K]}$

[2] We have derived the equation for vapor-liquid equilibrium which is the generally quoted form. An equivalent form expresses $\left(\frac{dp}{dT}\right)^{eq}$ for the equilibrium for chemical substance j in two phases α and β.

[3] C. Mosselman, W. H. van Vugt and H. Vos, J. Chem. Eng. Data 1982,**27**,246.

[4] From $dH = T\,dS + V\,dp$

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V$$
$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_T + V$$
$$\left(\frac{\partial H}{\partial p}\right)_T = T^{-1}\left(\frac{\partial V}{\partial T^{-1}}\right)_T + V$$
$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial\,(T^{-1}\,V)}{\partial T^{-1}}\right)_T$$

[5] L. Q. Lobo and A. G. M. Ferreira, J. Chem. Thermodyn., 2001,**33**,1597.

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1.14.10: Gibbs - Helmholtz Equation

The Gibbs energy and enthalpy of a closed system are related;

$$\mathrm{G} = \mathrm{H} - \mathrm{T}\,\mathrm{S}$$

The two properties G and H are also related by the Gibbs - Helmholtz equation through the dependence of G on temperature at fixed pressure. We envisage a situation in which a closed system at equilibrium having Gibbs energy G is displaced to a neighbouring equilibrium state by a change in temperature at constant pressure. We are interested in the partial derivative, $\left[\frac{\partial(\mathrm{G}/\mathrm{T})}{\partial \mathrm{T}}\right]_{\mathrm{p,A}=0}$. In general terms we consider the isobaric differential dependence of (G/T) on temperature.

$$\frac{\mathrm{d}}{\mathrm{dT}}\left(\frac{\mathrm{G}}{\mathrm{T}}\right)_{\mathrm{p}} = \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{p} - \frac{\mathrm{G}}{\mathrm{T}^2}$$

$$\mathrm{T}^2\frac{\mathrm{d}}{\mathrm{dT}}\left(\frac{\mathrm{G}}{\mathrm{T}}\right)_{\mathrm{p}} = \mathrm{T}\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{p}} - \mathrm{G}$$

But

$$\mathrm{S} = -\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

For an equilibrium change, equations (b) and (c) yield equation (e).

$$\mathrm{T}^2\frac{\mathrm{d}}{\mathrm{dT}}\left(\frac{\mathrm{G}}{\mathrm{T}}\right)_{\mathrm{p}} = -(\mathrm{G} + \mathrm{T}\,\mathrm{S})$$

But $\mathrm{H} = \mathrm{G} + \mathrm{T}\,\mathrm{S}$. Then,

$$\mathrm{H} = -\mathrm{T}^2\frac{\mathrm{d}}{\mathrm{dT}}\left(\frac{\mathrm{G}}{\mathrm{T}}\right)_{\mathrm{p}}$$

For an equilibrium change,

$$\Delta\mathrm{H}(\mathrm{A}=0) = -\mathrm{T}^2\frac{\mathrm{d}}{\mathrm{dT}}\left(\frac{\Delta\mathrm{G}}{\mathrm{T}}\right)_{\mathrm{p;A}=0}$$

or,

$$\Delta\mathrm{H}(\mathrm{A}=0) = \frac{\mathrm{d}}{\mathrm{dT}^{-1}}\left(\frac{\Delta\mathrm{G}}{\mathrm{T}}\right)_{\mathrm{p;A}=0}$$

In a similar manner we obtain the Gibbs -Helmholtz equation for a system perturbed at constant composition [1].

$$\Delta\mathrm{H}(\text{ fixed }\xi) = \frac{\mathrm{d}}{\mathrm{dT}^{-1}}\left(\frac{\Delta\mathrm{G}}{\mathrm{T}}\right)_{\mathrm{p},\bar{\xi},}$$

Equation (f) is the starting point for the development of another important equation. Thus,

$$\mathrm{H} = -\mathrm{T}^2\left[-\frac{\mathrm{G}}{\mathrm{T}^2} + \frac{1}{\mathrm{T}}\frac{\mathrm{dG}}{\mathrm{dT}}\right]$$

Hence,

$$\mathrm{H} = \mathrm{G} - \mathrm{T}\left[\frac{\mathrm{dG}}{\mathrm{dT}}\right]$$

Equation (k) is differentiated with respect to temperature at constant pressure and at '$\mathrm{A}=0$'.

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p,A}=0} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{p,A}=0} - \mathrm{T}\left(\frac{\partial^2 \mathrm{G}}{\partial \mathrm{T}^2}\right)_{p,A=0} - \left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{p,A}=0}$$

Hence,

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p,A=0}} = -\mathrm{T}\left(\frac{\partial^2 \mathrm{G}}{\partial \mathrm{T}^2}\right)_{\mathrm{p,A=0}}$$

But

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,A=0} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right) = -\left(\frac{\partial S}{\partial T}\right)_{p,A=0}$$

Also the equilibrium isobaric heat capacity,

$$C_p(A=0) = \left(\frac{\partial H}{\partial T}\right)_{p,A=0}$$

Equations (m), (n) and (o) yield equation (p).

$$\left(\frac{\partial S}{\partial T}\right)_{p,A=0} = \frac{C_p(A=0)}{T}$$

Equation (p) relates the isobaric equilibrium dependence of entropy of a closed system on temperature to the isobaric heat capacity. Also starting from, $\mathrm{H = G + T\,S}$, then

$$(\partial \mathrm{H}/\partial \mathrm{p})_{\mathrm{T}} = (\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T}} + \mathrm{T}\,(\partial \mathrm{S}/\partial \mathrm{p})_{\mathrm{T}}$$

Using a Maxwell Equation,

$$(\partial H/\partial p)_T = \mathrm{V} - \mathrm{T}\,(\partial \mathrm{V}/\partial \mathrm{T})_{\mathrm{p}}$$

Similarly,

$$(\partial \mathrm{U}/\partial \mathrm{T})_{\mathrm{V}} = \mathrm{C_V} = \mathrm{T}\,(\partial \mathrm{S}/\partial \mathrm{T})_{\mathrm{V}}$$

And

$$(\partial \mathrm{U}/\partial \mathrm{V})_{\mathrm{T}} = -\mathrm{p} - \mathrm{T}\,(\partial \mathrm{V}/\partial \mathrm{T})_{\mathrm{p}}\,(\partial \mathrm{p}/\partial \mathrm{V})_{\mathrm{T}}$$

Footnote

[1] There are many thermodynamic equations which are of the GibbsHelmholtz type. As a common feature they conform to the following calculus property.

Given

$$\mathrm{f = f(x, y)}$$

Then

$$\left(\frac{\partial (f/x)}{\partial (1/x)}\right)_y = -x^2\left(\frac{\partial (f/x)}{\partial x}\right)_y = f - x\left(\frac{\partial f}{\partial x}\right)_y$$

Similarly,

$$\left(\frac{\partial (f/y)}{\partial (1/y)}\right)_x = -y^2\left(\frac{\partial (f/x)}{\partial y}\right)_x = f - y\left(\frac{\partial f}{\partial y}\right)_x$$

Normally f stands for a thermodynamic potential and x and y $for its natural variables. Thus a total of 8 equations of the Gibbs - Helmholtz type holding for closed systems can be constructed from \(\mathrm{U = U(S, V), F = F(T, V), H = H(S, p)}$ and $\mathrm{G = G(T, p)}$.

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1.14.11: Guggenheim-Scatchard Equation / Redlich-Kister Equation

For binary liquid mixtures at fixed T and p, an important task is to fit the dependence of ${\mathrm{G_m}}^{\mathrm{E}}$ on x_2 to an equation in order to calculate the derivative $\mathrm{d{G_m}^E/dx_2}$ at required mole fractions. The **Guggenheim-Scatchard** [1,2] (commonly called the **Redlich-Kister** [3]) equation is one such equation. This equation has the following general form.

$$\mathrm{X_m^E = x_2\,(1-x_2)\sum_{i=1}^{i=k} A_i\,(1-2x_2)^{i-1}} \tag{1.14.11.1}$$

$\mathrm{A_i}$ are coefficients obtained from a least squares analysis of the dependence of ${\mathrm{G_m}}^{\mathrm{E}}$ on x_2. The equation clearly satisfies the condition that ${\mathrm{G_m}}^{\mathrm{E}}$ is zero at $x_2 = 0$ and at $x_2 = 1$. In fact the first term in the $\mathrm{G-S}$ equation has the following form.

$$X_m^E = x_2\,(1-x_2)\,A_1 \tag{1.14.11.2}$$

According to Equation 1.14.11.2 ${\mathrm{X_m}}^{\mathrm{E}}$ is an extremum at $x_2 = 0.5$, the plot being symmetric about the line from ${\mathrm{X_m}}^{\mathrm{E}}$ to '$x_2 = 0.5$'. In fact for most systems the $\mathrm{A_1}$ term is dominant. For the derivative $\mathrm{dG_m^E/dx_2}$, we write Equation 1.14.11.1 in the following general form.

$$\mathrm{X_m^E = \left(x_2 - x_2^2\right) Q} \tag{1.14.11.3}$$

Then

$$\mathrm{dX_m^E/x_2 = x_2\,(1-x_2)\,dQ/dx_2 + (1-2x_2)\,Q} \tag{1.14.11.4}$$

where

$$\mathrm{dQ/dx_2 = -2\sum_{i=2}^{i=k}(i-1)A_i\,(1-2x_2)^{i-2}} \tag{1.14.11.5}$$

Equation 1.14.11.1 fits the dependence with a set of contributing curves which all pass through points, ${\mathrm{X_m}}^{\mathrm{E}} = 0$ at $x_1 = 0$ and $x_1 = 1$. The usual procedure involves fitting the recorded dependence using increasing number of terms in the series, testing the statistical significance of including a further term. Although Equation 1.14.11.1 has been applied to many systems and although the equation is easy to incorporate into computer programs using packaged least square and graphical routines, the equation suffers from the following disadvantage. As one incorporates a further term in the series, (e.g. A_j) estimates of all the previously calculated parameters (i.e. $\mathrm{A_2}$, $\mathrm{A_3}$, ... A_{j-1}) change. For this reason orthogonal polynomials have been increasingly favoured especially where the appropriate computer software is available. The only slight reservation is that derivation of explicit equations for the required derivative $\mathrm{dX_m^E}$ is not straightforward. The problem becomes rather more formidable when the second and higher derivatives are required. The derivative $\mathrm{d^2X_m^E}$ is sometimes required by calculations concerning the properties of binary liquid mixtures.

The derivative $\mathrm{dG_m^E/dx_1}$ and ${\mathrm{G_m}}^{\mathrm{E}}$ are combined (see Topic EZ20) to yield an equation for $\mathrm{ln\,(f_1)}$.

$$\ln(f_1) = \frac{G_m^E}{RT} + \frac{(1-x_1)}{RT}\frac{dG_m^E}{dx_1} \tag{1.14.11.6}$$

A similar equation leads to estimates of $\mathrm{ln\,(f_2)}$. Hence the dependences are obtained of both $\mathrm{ln\,(f_1)}$ and $\mathrm{ln\,(f_2)}$ on mixture composition. It is of interest to explore the case where the coefficients $\mathrm{A_2}$, $\mathrm{A_3}$ ... in Equation 1.14.11.1 are zero. Then

$$\mathrm{X_m^E = x_2\,(1-x_2)\,A_1} \tag{1.14.11.7}$$

and

$$\mathrm{dX_m^E/dx_2 = (1-2x_2)\,A_1} \tag{1.14.11.8}$$

With reference to the Gibbs energies,

$$\mathrm{ln\,(f_2) = (1/RT)\left[x_2\,(1-x_2) + (1-x_2)\,(1-2x_2)\right]A_1^G} \tag{1.14.11.9}$$

$$\ln(f_2) = \left(A_1^G/RT\right)\left[1 - 2x_2 + x_2^2\right] \tag{1.14.11.10}$$

or,

$$\ln(f_2) = \left(A_1^G/RT\right)[1 - x_2]^2 \tag{1.14.11.11}$$

In fact the equation reported by Jost et al. [4] has this form.

Rather than using the Redlich-Kister equation, recently attention has been directed to the **Wilson equation** [5] written in Equation 1.14.11.12 for a two-component liquid [6].

$$G_m^E/RT = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \tag{1.14.11.12}$$

Then , for example [7],

$$\ln(f_1) = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{1.14.11.13}$$

The Wilson equation forms the basis for two further developments, described as the NRTL (non-random, two-liquid) equation [8-10] and the UNIQUAC equation [9-10].

Footnotes

[1] E. A. Guggenheim, Trans. Faraday Soc.,1937,**33**,151; equation 4.1.

[2] G. Scatchard, Chem. Rev.,1949,**44**,7;see page 9.

[3] O. Redlich and A. Kister, Ind. Eng. Chem.,1948,**40**,345; equation 8.

[4] F. Jost, H. Leiter and M. J. Schwuger, Colloid Polymer Sci., 1988, **266**, 554.

[5] G. M. Wilson, J. Am. Chem. Soc.,1964,**86**,127.

[6] See also

a. R. V. Orye and J. M. Prausnitz, Ind. Eng. Chem.,1965,**57**,19.
b. S. Ohe, Vapour-Liquid Equilibrium Data, Elsevier, Amsterdam, 1989.

[7] From Equation 1.14.11.12,

$$\frac{1}{RT}\frac{dG_m^E}{dx_1} = -\ln(x_1 + \Lambda_{12}x_2) - \frac{x_1(1 - \Lambda_{12})}{x_1 + \Lambda_{12}x_2} + \ln(\Lambda_{21}x_1 + x_2) - \frac{x_2(\Lambda_{21} - 1)}{\Lambda_{21}x_1 + x_2}$$

Then using Equation 1.14.11.6 with $1 - x_1 = x_2$,

$$\ln(f_1) = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(\Lambda_{21}x_1 + x_2) - x_2 \ln(x_1 + \Lambda_{12}x_2) - \frac{x_1x_2(1 - \Lambda_{12})}{x_1 + \Lambda_{12}x_2} + x_2 \ln(\Lambda_{21}x_1 + x_2) + \frac{(x_2)^2(1 - \Lambda_{21})}{\Lambda_{21}x_1 + x_2}$$

Or,

$$\ln(f_1) = -(x_1 + x_2)\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}x_1 - x_1}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}x_2 - x_2}{\Lambda_{21}x_1 + x_2}\right]$$

But

$$\Lambda_{12}x_1 - x_1 = \Lambda_{12}(1 - x_2) - x_1 = \Lambda_{12} - (x_1 + \Lambda_{12}x_2)$$

Hence,

$$\ln(f_1) = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12} - (x_1 - \Lambda_{12}x_2)}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21} - (\Lambda_{21}x_1 + x_2)}{\Lambda_{21}x_1 + x_2}\right]$$

Or,

$$\ln(f_1) = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

[8] D. Abrams and J. M. Prausnitz, AIChE J.,1975,**21**,116.

[9] R. C. Reid, J. M. Prausnitz and E. B. Poling, The Properties of Gases and Liquids, McGraw-Hill, New York, 4th edn.,1987, chapter 8.

[8] J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, Molecular Themodyanamics of Fluid Phase Equilibria, Prentice – Hall, Upper Saddle River, N.J., 3rd edn.,1999,chapter 6.

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1.14.12: Legendre Transformations

Many important thermodynamic equations are closely related. These relationships are often highlighted by the mathematical technique, Legendre Transformations [1,2]. With reference to thermodynamics, Callen [3] discusses application of Legendre Transformations. The essential features of Legendre Transformations can be understood in the following terms.

A primary variable Q is defined by two dependent variables x and y. Thus

$$Q = Q[x, y]$$

Then

$$\mathrm{dQ} = \left(\frac{\partial \mathrm{Q}}{\partial \mathrm{x}}\right)_{\mathrm{y}} \mathrm{dx} + \left(\frac{\partial \mathrm{Q}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \mathrm{dy}$$

By definition,

$$\mathrm{u} = \left(\frac{\partial \mathrm{Q}}{\partial \mathrm{x}}\right)_{\mathrm{y}} \quad \text{and} \quad \mathrm{v} = \left(\frac{\partial \mathrm{Q}}{\partial \mathrm{y}}\right)_{\mathrm{x}}$$

Then from equation (b),

$$\mathrm{dQ} = \mathrm{u}\,\mathrm{dx} + \mathrm{v}\,\mathrm{dy}$$

A new variable Z is defined by equation (e).

$$\mathrm{Z} = \mathrm{Z[u, y]} \text{ where } \mathrm{Z} = \mathrm{Q} - \mathrm{u}\,\mathrm{x}$$

Then,

$$\mathrm{dZ} = \mathrm{dQ} - \mathrm{x}\,\mathrm{du} - \mathrm{u}\,\mathrm{dx}$$

Hence using equation (d),

$$dZ = u\,dx + v\,dy - x\,du - u\,dx$$

Or,

$$\mathrm{d}Z = -\mathrm{x}\,\mathrm{du} + \mathrm{v}\,\mathrm{dy}$$

Hence,

$$x = -\left(\frac{\partial Z}{\partial u}\right)_{y} \quad \text{and} \quad v = \left(\frac{\partial Z}{\partial y}\right)_{u}$$

Comparison of equations (a) and (e) reveals the transformation, $\mathrm{Q[x, y]} \rightarrow \mathrm{Z[u, y]}$. We now explore thermodynamic transformations [3]. The following Master Equation relates the change in thermodynamic energy U with the changes in entropy S at temperature T, volume V at pressure p and composition ξ at affinity A; $\mathrm{U} = \mathrm{U[S, V, \xi]}$.

$$\mathrm{dU} = \mathrm{T}\,\mathrm{dS} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi$$

By definition, enthalpy $\mathrm{H} = \mathrm{U} + \mathrm{p}\,\mathrm{V}$;

$$\mathrm{dH} = -\mathrm{dU} + \mathrm{p}\,\mathrm{dV} + \mathrm{V}\,\mathrm{dp}$$

Using equation (j),

$$\mathrm{dH} = \mathrm{T}\,\mathrm{dS} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi + \mathrm{p}\,\mathrm{dV} + \mathrm{V}\,\mathrm{dp}$$

Then $\mathrm{dH} = \mathrm{T}\,\mathrm{dS} + \mathrm{V}\,\mathrm{dp} - \mathrm{A}\,\mathrm{d}\xi$ Or,

$$\mathrm{H} = \mathrm{H[S, p, \xi]}$$

The transformation is- $\mathrm{U[S, V, \xi]} \rightarrow \mathrm{H[S, p, \xi]}$ By definition, Gibbs energy

$$\mathrm{G} = \mathrm{U} + \mathrm{p}\,\mathrm{V} - \mathrm{T}\,\mathrm{S}$$

Or using equation (k),

$$G = H - T\,S$$

Then

$$dG = dH - T\,dS - S\,dT$$

Hence from equation (l)

$$dG = T\,dS + V\,dp - A\,d\xi - T\,dS - S\,dT$$

Or, $dG = -S\,dT + V\,dp - A\,d\xi$ And,

$$G = G[T, p, \xi]$$

The transformation is $H[S, p, \xi] \rightarrow G[T, p, \xi]$ Similarly, $U[S, V, \xi] \rightarrow F[T, V, \xi]$ Ledgendre transformations can be examined in the broad context of chemistry and biochemistry [5]. Their importance lies in establishing the general mathematical structure of thermodynamics [6].

Footnotes

[1] A. M. Legendre; an eighteenth century mathematician.

[2] C. Paus at http://web.mit.edu /8.21/www/ notes/notes/ node7.html

[3] B. Callen, Thermodynamics, Wiley, New York,1961.

[4] E. Grunwald, Thermodynamics of Molecular Species, Wiley, New York , 1997.

[5] R. A. Alberty, Chem. Revs.,1994,**94**,1457.

[6] D. Kondepudi and I. Prigogine, Modern Thermodynamics, Wiley, New York,1998.

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1.14.13: Closed System

A closed system is effectively a closed reaction vessel. As chemists we are interested in changes in chemical composition of the closed system. The condition “closed” means that while observing the processes taking place inside the system, we do not add more chemical substances to the system from the surroundings or remove chemical substance from the system into the surroundings. Actually the thermodynamic treatment of closed systems is simpler than for other systems. The system and surroundings interact by virtue of, for example, heat passing between system and surroundings.

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1.14.14: Cohesive Energy Density

The molar enthalpy of vaporisation $\Delta_{\rm vap}\,{\rm H}^*$ is the change in enthalpy for one mole of chemical substance j on going from the liquid to the (perfect) gaseous state. The properties of a given liquid-j are determined by $j-j$ intermolecular forces. By definition, there are no intermolecular forces in a perfect gas. Hence $\Delta_{\rm vap}{\rm H}^*_{\rm j}(\ell)$ offers an insight into the strength of intermolecular forces in the liquid state. We have to be careful not to use the word 'energy'. By definition enthalpy ${\rm H}$ equals (${\rm U}+{\rm p}\,{\rm V}$). For phase I at temperature ${\rm T}$ and pressure ${\rm p}$,

$$\mathrm{U}^*_{\rm j}(\mathrm{I}) = \mathrm{H}^*_{\rm j}(\mathrm{I}) - \mathrm{p}\,\mathrm{V}^*_{\rm j}(\mathrm{I})$$

$$\text{Similarly for phase II, } \mathrm{U}^*_{\rm j}(\mathrm{II}) = \mathrm{H}^*_{\rm j}(\mathrm{II}) - \mathrm{p}\,\mathrm{V}^*_{\rm j}(\mathrm{II})$$

$$\text{Hence,}\quad U^*_j(\,\mathrm{II}\,) - U^*_j(I) = H^*_j(\,\mathrm{II}\,) - H^*_j(I) - p\,\left[V^*_j(\,\mathrm{II}\,) - V^*_j(I)\right]$$

If phase II is a perfect gas and phase I is the corresponding liquid, $\mathrm{V}^*_{\rm j}(\mathrm{II}) >> \mathrm{V}^*_{\rm j}(\mathrm{I})$; for one mole of chemical substance j, $\mathrm{p}\,\mathrm{V}^*_{\rm j}(\mathrm{II}) = \mathrm{R}\,\mathrm{T}$.

$$\text{Consequently } \Delta_{\rm vap}\,\mathrm{U}^*_{\rm j}(\,\mathrm{T}) = \Delta_{\rm vap}\mathrm{H}^*_{\rm j}(\,\mathrm{T}) - \mathrm{R}\,\mathrm{T}$$

$\Delta_{\rm vap}\,\mathrm{U}^*_{\rm j}(\,\mathrm{T})$ is the molar thermodynamic energy of vaporisation for liquid j at temperature ${\rm T}$. Having calculated $\Delta_{\rm vap}\,\mathrm{H}^*_j(\,\mathrm{T})$ from experimental data we obtain $\Delta_{\rm vap}\,U^*_j(T)$, a measure of the strength of inter-molecular interactions in the liquid.

The differential quantity $(\partial{\rm U}/\partial{\rm V})_{\rm T}$ defines the internal pressure $\pi_{int}(j)$ of chemical substance j. For liquid j,

$$\pi^*_{\rm int}(\ell;\mathrm{j}) = \left[\partial\mathrm{U}^*_{\rm j}(\ell)/\partial\mathrm{V}^*_{\rm j}(\ell)\right]_{\rm T}$$

The internal pressure for liquids, of the order 10^8 Pa, is an indicator of the strength of intermolecular forces [1]. The structure of the terms in equation (e) prompts a slight rewrite using properties that are either readily measured or calculated, namely $\Delta_{\rm vap}\,\mathrm{U}^*_{\rm j}(\,\mathrm{T})$ and the molar volume of the liquid at temperature T, $\mathrm{V}^*_{\rm j}(\,\mathrm{T})$ [2,3]. The result is the cohesive energy density, c.e.d., a measure of the cohesion within a liquid.

$$\text{By definition, c.e.d. } = \Delta_{\rm vap}\,\mathrm{U}^*_{\rm j}(\,\mathrm{T})/\mathrm{V}^*_{\rm j}(\ell)$$

Intuitively, $\Delta_{\rm vap}\,\mathrm{U}^*_{\rm j}(\,\mathrm{T})$ is a measure of cohesive interactions in the liquid whereas volume is a measure of the repulsive interactions, keeping the molecules in the liquid apart. At constant $\Delta_{\rm vap}\,\mathrm{U}^*_{\rm j}(\,\mathrm{T})$, c.e.d decreases with increase in molar volume; c.f. repulsion. But at constant $\mathrm{V}^*_{\rm j}(\,\mathrm{T})$, c.e.d. increases with increase in $\Delta_{\rm vap}\,\mathrm{U}^*_j(\,\mathrm{T})$, the attractive part.

$$\text{If the vapour is a perfect gas, c.e.d. } = \left[\Delta_{\rm vap}\mathrm{H}^*_{\rm j}(\ell) - \mathrm{R}\,\mathrm{T}\right]/\mathrm{V}^*_{\rm j}(\ell)$$

If the molar mass of the liquid j equals M_j and the density equals $\rho^*_{\rm j}(\ell)$

$$\text{c.e.d. } = \left[\Delta_{\rm vap}\mathrm{H}^*_{\rm j}(\ell) - \mathrm{R}\,\mathrm{T}\right]\,\rho^*_{\rm j}(\ell)/\mathrm{M_j}$$

M_j is expressed in kgmol^{-1} and $\rho^*_{\rm j}(\ell)$ in kgm^{-3}, consistent with c.e.d. being expressed in ($\mathrm{Jmol}^{-1}\,\mathrm{m}^{-3}$). At 298.2 K, $\mathrm{R}\,\mathrm{T} = 2.48\ \mathrm{kJ\ mol}^{-1}$. The ratio of internal pressure $\pi_{\rm int}\,(\mathrm{j})$ to c.e.d. defines a property n using equation (i).

$$\mathrm{n} = \left[\partial\mathrm{U}^*_{\rm j}(\ell)/\partial\mathrm{V}^*_{\rm j}(\ell)\right]_{\rm T} / \left[\Delta_{\rm vap}\mathrm{U}^*_{\rm j}(\ell)/\mathrm{V}^*_{\rm j}(\ell)\right]$$

The dimensionless ratio n has been used to comment on the strength of intermolecular forces in a liquid [4].

In the context of the properties of liquid mixtures, using the definition of enthalpy $\mathrm{H}(=\mathrm{U}+\mathrm{p}\,\mathrm{V})$ we can write the following equation for a given phase I containing n_1 moles of substance 1 and n_2 moles of substance 2.

$$\mathrm{U}\,(\mathrm{I};\mathrm{n}_1+\mathrm{n}_2) = \mathrm{H}\,(\mathrm{I};\mathrm{n}_1+\mathrm{n}_2) - \mathrm{p}\,\mathrm{V}\,(\mathrm{I};\mathrm{n}_1+\mathrm{n}_2)$$

We assert that phase I is an ideal binary liquid mixture. Then,

$$\begin{aligned}&\mathrm{U}\,(\mathrm{I};\mathrm{n}_1+\mathrm{n}_2;\mathrm{mix};\mathrm{id}) = \\ &\quad \mathrm{n}_1\,\mathrm{H}^*_1(\ell) + \mathrm{n}_2\,\mathrm{H}^*_2(\ell) - \mathrm{p}\,\mathrm{V}\,(\mathrm{I};\mathrm{n}_1+\mathrm{n}_2;\ \mathrm{mix}\ ;\mathrm{id})\end{aligned}$$

We assert that phase II is a perfect gas comprising n_1 moles of substance 1 and n_2 moles of substance 2. Then

$$\mathrm{U\,(II; n_1 + n_2; pfg)} = \mathrm{n_1\,H_1^*(pfg) + n_2\,H_2^*(pfg) - p\,V\,(II; n_1 + n_2; pfg)}$$

$$\text{For a perfect gas, } \mathrm{p\,V\,(II; n_1 + n_2; pfg) = (n_1 + n_2)\,R\,T}$$

We express the thermodynamic energy of vaporisation for $(n_1 + n_2)$ moles passing from phase I to phase II.

$$\mathrm{\Delta_{vap}\,U\,(id, n_1 + n_2) = n_1\,\Delta_{vap}\,H_1^* + n_2\,\Delta_{vap}H_2^* - (n_1 + n_2)\,R\,T + p\,V\,(I; n_1 + n_2;\ mix;\ id\ )}$$

Therefore for one mole,

$$\mathrm{\Delta_{vap}\,U_m(id) = x_1\,\Delta_{vap}\,H_1^* + x_2\,\Delta_{vap}\,H_2^* - R\,T + p\,V_m(I; mix; id)}$$

Suppose however that the thermodynamic properties of the liquid mixture are not ideal. We rewrite equation (k) in the following form (for one mole of mixture) where H_m^E and V_m^E are the excess molar enthalpies and excess molar volumes of mixing.

$$\mathrm{U_m(I, mix) = \left[x_1\,H_1^*(\ell) + x_2\,H_2^*(\ell) + H_m^E\right] - p\,\left[x_1\,V_1^*(\ell) + x_2\,V_2^*(\ell) + V_m^E\right]}$$

$$\mathrm{Or\ U_m(I, mix) = \left[x_1\,H_1^*(\ell) + x_2\,H_2^*(\ell) + H_m^E\right] - p\,V_m(mix)}$$

Therefore the molar thermodynamic energy of vaporisation on going from the real mixture to the perfect gas in given by equation (r).

$$\mathrm{\Delta_{vap}\,U_m = \left[x_1\,\Delta_{vap}\,H_1^*(\ T) + x_2\,\Delta_{vap}\,H_2^*(\ T) - H_m^E\right] - R\,T + p\,V_m(mix)}$$

The cohesive energy density, c.e.d., for a real binary liquid mixture is given by equation (s).

$$\mathrm{c.e.d.\ = \{[x_1\,\Delta_{vap}H_1^*(\ T) + x_2\ \ \Delta_{vap}H_2^*(\ T) - H_m^E]\,/V_m(mix)\} - \{R\,T/V_m(mix)\} + p}$$

The c.e.d. for a given binary mixture is given by the molar enthalpies of vaporisation of the pure components, the excess molar enthalpy of mixing and the molar volume of the mixture. For the corresponding ideal binary mixture, c.e.d.(id) is given by equation (t).

$$\mathrm{c.e.d.(id)} = \mathrm{\{[x_1\,\Delta_{vap}\,H_1^*(\ T) + x_2\ \ \Delta_{vap}\,H_2^*(\ T)]\,/V_m(mix; id)\} - \{R\,T/V_m(mix; id)\} + p}$$

The difference between $\mathrm{\Delta_{vap}\,U_m/V_m(mix)}$ and $\mathrm{\Delta_{vap}U_m/V_m(mix; id)}$ is the excess cohesive energy density, $(\ \text{c.e.d.}\ )^E$. The sign of $(\ \text{c.e.d.}\ )^E$ is controlled to a significant extent by the excess molar volume V_m^E and the excess molar enthalpy H_m^E [6]. In fact equations (s) and (t) lead to m equation (u).

$$(\ \text{c.e.d.}\ )^E = \frac{-[x_1\,\Delta_{vap}H_1^*(\ T) + x_2\,\Delta_{vap}H_2^*(\ T) - R\,T]}{V_m(mix)\,V_m(mix; id)} - \frac{H_m^E}{V_m(mix)}$$

Recently the cohesive energy density of a liquid has been described as a ‘solvation pressure’ acting on, for example, ethanol in ethanol + water and ethanol + trichloromethane liquid mixtures [7].

Footnotes

[1] M. R. J. Dack, Aust. J. Chem.,1976,**27**,779.

[2] $\text{c.e.d.} = [\mathrm{Jmol^{-1}}] / [\mathrm{m^3\ mol^{-1}}] = [\mathrm{Jm^{-3}}] = [\mathrm{Nm^{-2}}]$; the unit of pressure. $\mathrm{R\,T} = [\mathrm{JK^{-1}\ mol^{-1}}]\ [\mathrm{K}] = [\mathrm{Jmol^{-1}}]$

[3] A variety of units are used for cohesive energy densities. Despite the fact that there are good grounds for using the unit $\mathrm{Jm^{-3}}$, the commonly used unit is calories per $\mathrm{cm^3}$, \mathrm{cal cm}^{-3}\).

For liquids 298.15 K and ambient pressure.

Liquid	c.e.d./ calcm^{-3}
water	547
methanol	204
benzene	85
tetrachloromethane	74

[4] A. F. M. Barton, J.Chem.Educ.,1971, **48**,156.

[5] For comments on the role of cohesive energy densities of solvents and rates of disproportionation, see A.P. Stefani, J. Am. Chem. Soc., 1968,**90**,1694.

[6] For comments on cohesive energy densities of binary aqueous mixtures see,

a. D. D. Macdonald and J. B. Hyne, Can. J. Chem.,1971, **49**,611,2636.
b. D. D. Macdonald, Can. J. Chem.,1976, **54**,3559.

[7] N.W. A.van Uden, H. Hubel, D. A. Faux, A. C. Tanczos, B. Howlin and D. J. Dunstan, J. Phys.: Condens. Mater,2003,**15**,1577.

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1.14.15: Degree of Dissociation

A given aqueous solution is prepared using n_1^0 moles of water and n_A^0 moles of a weak acid HA. The composition of the solution at equilibrium (at fixed T and p) is described as follows.

	HA(aq)	$\rightleftharpoons$	H^+(aq)+	A'(aq)
At $t = 0$	n_A^0		0	0 mol
At equilibirium,	$n_A^0 - \xi^{\mathrm{eq}}$		ξ^{eq}	ξ^{eq} mol
or,	$\mathrm{n}_\mathrm{A}^0 \left[1 - \frac{\xi^{eq}}{\mathrm{n}_\mathrm{A}^0}\right]$		ξ^{eq}	ξ^{eq} mol
or.	$\mathrm{n}_\mathrm{A}^0 (1-\alpha)$		$\alpha\, \mathrm{n}_\mathrm{A}^0$	$\alpha\, \mathrm{n}_\mathrm{A}^0$ mol

If the volume of the system is $1\ \mathrm{dm}^3$ then, $\mathrm{c}_\mathrm{A}^0 (1-\alpha) \quad \alpha\, \mathrm{c}_\mathrm{A}^0 \quad \alpha\, \mathrm{c}_\mathrm{A}^0 \quad \mathrm{moldm}^{-3}$

By definition, the degree of dissociation, $\alpha = \xi^{\mathrm{eq}}/\mathrm{n}_\mathrm{A}^0$; α is an intensive variable describing the 'degree' of dissociation. If the total volume of the solution is V, the concentration $\mathrm{c}_\mathrm{A}^0 = \mathrm{n}_\mathrm{A}^0/\mathrm{V}$. If the thermodynamic properties of the solution are ideal, the composition of the solution can be described by an equilibrium acid dissociation constant K_A.

$$\mathrm{K}_\mathrm{A} = \alpha^2\, \mathrm{c}_\mathrm{A}^0/(1-\alpha)$$

If

$$1 - \alpha \cong 1, \alpha^2 = \mathrm{K}_\mathrm{A}/\mathrm{c}_\mathrm{A}^0$$

If the acid is dibasic, the analysis is a little more complicated.

For an acid $\mathrm{H}_2\mathrm{A}$, there are two extents of acid dissociation.

	H_2A	$\rightleftharpoons$	H^++	HA^-
At $t = 0$,	n_A^0		0	0 mol
At equilibrium,	$\mathrm{n}_\mathrm{A}^0 - \xi_1$		$\xi_1 + \xi_2$	$\xi_1 - \xi_2$ mol
Or,	$n_A^0 \left[1 - \frac{\zeta_1}{n_A^0}\right]$		$\mathrm{n}_\mathrm{A}^0 \left[\frac{\xi_1}{\mathrm{n}_\mathrm{A}^0} + \frac{\xi_2}{\mathrm{n}_\mathrm{A}^0}\right]$	$\mathrm{n}_\mathrm{A}^0 \left[\frac{\xi_1}{\mathrm{n}_\mathrm{A}^0} - \frac{\xi_2}{\mathrm{n}_\mathrm{A}^0}\right]$ mol

By definition $\mathrm{c}_\mathrm{A}^0 = \mathrm{n}_\mathrm{A}^0/\mathrm{V}$ where V is the volume of solution expressed in dm^3. Also by definition $\alpha_1 = \xi_1/\mathrm{n}_\mathrm{A}^0$ and $\alpha_2 = \xi_2/\mathrm{n}_\mathrm{A}^0$

Hence from equation (d)

	H_2A	$\rightleftarrows$	H^++	\mathrm{HA}^{-}\)
At equilibrium,	$(\mathrm{n}_\mathrm{A}^0/\mathrm{V})\ [1-\alpha_1]$		$(\mathrm{n}_\mathrm{A}^0/\mathrm{V})\ [\alpha_1 + \alpha_2]$	$(\mathrm{n}_\mathrm{A}^0/\mathrm{V})\ [\alpha_1 - \alpha_2]$ mol
Or,	$\mathrm{c}_\mathrm{A}^0\ [1-\alpha_1]$		$\mathrm{c}_\mathrm{A}^0\ [\alpha_1 + \alpha_2]$	$\mathrm{c}_\mathrm{A}^0\ [\alpha_1 - \alpha_2]$ mol

	HA^-	$\rightleftarrows$	H^++	\mathrm{A}^{-2}\)
At $t = 0$,	0		0	0 mol
Also At equilibrium,	$\xi_1 - \xi_2$		$\xi_1 + \xi_2$	ξ_2 mol
Or,	$\mathrm{n}_\mathrm{A}^0 \left[\frac{\xi_1}{\mathrm{n}_\mathrm{A}^0} - \frac{\xi_2}{\mathrm{n}_\mathrm{A}^0}\right]$		$\mathrm{n}_\mathrm{A}^0 \left[\frac{\xi_1}{\mathrm{n}_\mathrm{A}^0} + \frac{\xi_2}{\mathrm{n}_\mathrm{A}^0}\right]$	$n_A^0 \left[\frac{\zeta_2}{n_A^0}\right]$ mol
	$\mathrm{c}_\mathrm{A}^0\ [\alpha_1 - \alpha_2]$		$\mathrm{c}_\mathrm{A}^0\ [\alpha_1 + \alpha_2]$	$\mathrm{c}_\mathrm{A}^0\, \alpha_2$

Total amount of \(\mathrm{H} in the system

$$= 2\ \left(\mathrm{n}_{\mathrm{A}}^{0} - \xi_1\right) + \xi_1 + \xi_2 + \xi_1 - \xi_2 = 2\,\mathrm{n}_{\mathrm{A}}^{0}$$

Total amount of A in the system

$$= \mathrm{n}_{\mathrm{A}}^{0} - \xi_1 + \xi_1 - \xi_2 + \xi_2 = \mathrm{n}_{\mathrm{A}}^{0}$$

If the thermodynamic properties of the solution are ideal,

$$\mathrm{K}_1 = \mathrm{c}_{\mathrm{A}}^{0}\ [\alpha_1 + \alpha_2]\ [\alpha_1 - \alpha_2] / [1 - \alpha_1]$$

If

$$\mathrm{K}_2 = 0, \alpha_2 = 0,\ \mathrm{K}_1 = \mathrm{c}_{\mathrm{A}}^{0}\ \alpha_1^2 / (1 - \alpha_1)$$

But

$$\mathrm{K}_2 = (\alpha_1 + \alpha_2)\ \alpha_2\, \mathrm{c}_{\mathrm{A}}^{0} / (\alpha_1 - \alpha_2)$$

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1.14.16: Energy and First Law of Thermodynamics

A central axiom of chemical thermodynamics is that a given system has a property called energy. In fact the First Law of Thermodynamics centres on the concept of energy. In its broadest terms, the law requires that the energy of the universe is constant [1]. This is a rather overwhelming statement. A more attractive statement is that the thermodynamic energy U of a typical chemistry laboratory is constant.

$$\mathrm{U} = \text{ constant} \tag{1.14.16.1}$$

The latter is the principle of conservation of energy; energy can be neither created nor destroyed. A chemist 'watches' energy "move" between system and surroundings. As a consequence of Equation 1.14.16.1 we state that,

$$\Delta\mathrm{U}(\text{ system }) = -\Delta\mathrm{U}(\text{ surroundings }) \tag{1.14.16.2}$$

We cannot know the actual energy U of a closed system although we agree that it is an extensive property of a system. In describing the energy changes we need a convention. We use the acquisitive convention, describing all changes in terms of how the system is affected. Thus $\Delta\mathrm{U} < 0$, means that the energy of the system falls whereas $\Delta\mathrm{U} > 0$ means that the energy increases [2]. In the context of chemistry, chemists agree that the energy of a given closed system can be increased in two ways:

i. heat q passing from the surroundings into the system, and
ii. work w done by the surroundings on the system. In a wider context the concept of energy is linked with the First Law of Thermodynamics which is based on the following axiom.

$$\Delta\mathrm{U} = \mathrm{q} + \mathrm{w} \tag{1.14.16.3}$$

As it stands the symbols U, q and w seem rather uninformative. It is the task of chemists to flesh out the meaning of these terms. If only '$\mathrm{p-V}$' work is involved,

$$\mathrm{w} = -\mathrm{p}\,\mathrm{dV} \tag{1.14.16.4}$$

The point of Equation 1.14.16.3 is to separate the work term from the heat term. The significance for chemists is that q links to the Second Law of Thermodynamics. Thus chemists know that heat flows spontaneously from high to low temperatures. This concept of 'spontaneous change' is picked up with enormous impact in the second law.

Footnotes

[1] Peter Atkins (Galileo's Finger, Oxford University press, 2003, page 107) speculates that the total energy of the universe 'may be exactly zero'.

[2] In principle it is possible to calculate the total energy of a given system using a scale in conjunction with Einstein's famous equation, $\mathrm{E} = \mathrm{m}\,\mathrm{c}^2$. However the mass corresponding to $1\ \mathrm{kJ}$ is only about $10^{-14}\ \mathrm{kg}$.

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1.14.17: Energy and Entropy

This Topic takes a rather different approach from the other Topics in this Notebook. Across the galaxy of terms used in thermodynamics, two terms stand out, namely **Energy** and **Entropy**. With respect to a given closed system, both terms describe extensive properties, using the letter U to identify energy and the letter S to identify entropy.

The term 'energy' is used quite generally in everyday life. One dictionary [1] describes energy as 'the power and ability to be physically active'. Perhaps we might not be too happy at the use of the term 'power' in this context on the grounds that this term is normally linked to the rate at which energy is supplied [2]. Indeed in every day life we refer to powerful engines in, for example, fast sports cars. Nevertheless in a thermodynamic context the concepts of **energy** and **energy change** are part of the language of chemistry; e.g. bond energy, energy of activation, radiant energy… The First Law of Thermodynamics formalises the concept of energy change using the following ostensibly simple equation.

$$\Delta \mathrm{U} = \mathrm{q} + \mathrm{w}$$

Here U is the thermodynamic energy, a function of state; $\Delta \mathrm{U}$ describes the increase in thermodynamic energy of a closed system when heat q flows from the surroundings into a given system and work w is done by the surroundings on that system.

The distinction between heat and work is crucial. There are many ways in which the surroundings can do work on a system. Caldin [3] lists many examples in which work is given by the product of Intensity and Capacity Factors; e.g. intensity factor pressure, p and capacity factor volume, V such that $\mathrm{w} = \mathrm{p}\,\mathrm{dV}$.

In the context of energy, chemical thermodynamics quite generally describes quite modest changes in energy. Even in the case of an explosion involving, for example, ignition of a mixture of hydrogen and oxygen gases, the energy change turns out to involve transitions between electronic energy levels in atoms and molecules. Much more dramatic are nuclear reactions which involve the conversion of mass, m into energy E as described by Einstein's famous equation.

$$\mathrm{E} = \mathrm{m}\,\mathrm{c}^2$$

Here c is the speed of light, $3.00 \times 10^8\ \mathrm{ms}^{-1}$. In nuclear fission the nucleus of an atom breaks into two smaller nuclei of similar mass [4]. Thus $\mathrm{uranium}^{235}$ nuclei bombarded by neutrons split into barium-142 and krypton-92 nuclei. Einstein's equation shows that $1.0\ \mathrm{g}$ of this uranium isotope undergoes fission with the release of 7.5×10^{10} J [5], an awesome amount of energy.

Here we return to the domain of chemical properties and chemical reactions where nuclei of atoms are not destroyed. Our interest centres on the thermodynamic variable, entropy S, an extensive function of state. However in every day conversation and in articles in newspapers and magazines the term 'entropy' is rarely used suggesting that it is not important. This conclusion is incorrect and the message quite misleading.

In these Topics we describe the Second Law using an equation based on the formulation given by Clausius as follows.

$$\mathrm{T}\,\mathrm{dS} = \mathrm{q} + \mathrm{A}\,\mathrm{d}\xi$$

Here a positive q describes heat passing from the surroundings into a closed system; A is the affinity for spontaneous change, the change being described by the property ξ. Following De Donder [6] as discussed by Prigogine and Defay [7] the Second Law is simply stated as follows.

$$A\,d\xi \geq 0$$

For a system moving between equilibrium states (i.e. the system and surroundings are at all stages at equilibrium where A is zero),

$$\mathrm{T}\,\mathrm{dS} = \mathrm{q}$$

Hence q, measured using a calorimeter, is a direct measure of the change in entropy accompanying a change where the system is always in equilibrium with the surroundings. In fact this statement provides a useful answer to the question 'what is entropy?'. There is therefore a fundamental link between the two quantities dS and heat q. Indeed we understand immediately the importance of calorimeters in thermodynamics. At the same time we understand the importance of chemical kinetics because this subject is built around equation (d) which in the basis of the Law of Mass Action.

In summary we see how the two foundation stones of thermodynamics, namely energy and entropy, are formalised in two laws for which there are no exceptions. So we can end the Topics here. But chemists do not although there are new hazards.

It follows from equation (d) that for a process where $\mathrm{q} < 0$, the entropy of the system decreases. [It is interesting to note that the unit of entropy $\mathrm{mathm}JK^{-1}$ is the same as that for heat capacity.] At this point we review the arguments advanced by Lewis and Randall [8].

An important reference system in thermodynamics is the perfect gas. No such gas is actually known in the real world but the concept is very valuable. The properties of a perfect gas conform to the two laws [7b].

We envisage a closed system, volume V containing n moles of a perfect gas. The first condition states that the thermodynamic energy U is only a function of temperature. Thus,

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = 0$$

The second condition states that the following equation relates the pressure, volume and temperature of n moles of a perfect gas.

$$\mathrm{p\,V} = \mathrm{n\,R\,T}$$

Thus for one mole of a perfect gas, having molar volume $\mathrm{V_m}$,

$$\mathrm{p\,V_m} = \mathrm{R\,T}$$

A key equation (Topic 2500) relates the change in thermodynamic energy U to the changes in entropy, volume and composition. Thus

$$\mathrm{dU} = \mathrm{T\,dS} - \mathrm{p\,dV} - \mathrm{A\,d}\xi$$

For an equilibrium transformation, the affinity of spontaneous change is zero. Hence for an equilibrium process,

$$\mathrm{dU} = \mathrm{T\,dS} - \mathrm{p\,dV}$$

For 1 mole of an ideal gas,

$$\mathrm{dU_m} = \mathrm{T\,dS_m} - \mathrm{p\,dV_m}$$

Or,

$$\mathrm{dS_m} = \frac{1}{\mathrm{T}}\,\mathrm{dU_m} + \frac{\mathrm{P}}{\mathrm{T}}\,\mathrm{dVm_m}$$

Molar isochoric heat capacity $\mathrm{C_{Vm}}$ is related to $\mathrm{dU_m}$ by equation (m).

$$\mathrm{C_{V_m}} = (\partial \mathrm{U_m}/\partial \mathrm{T})_{\mathrm{V(m)}}$$

Then,

$$\mathrm{dS_m} = \frac{\mathrm{C_{Vm^m}}}{\mathrm{T}}\,\mathrm{dT} + \frac{\mathrm{p}}{\mathrm{T}}\,\mathrm{dVV_m}$$

We define the molar entropy of an ideal gas using equation (o).

$$\mathrm{S_m} = \mathrm{S_m}\,[\mathrm{T}, \mathrm{V_m}]$$

The total differential of equation (o) takes the following form.

$$\mathrm{dS_m} = \left(\frac{\partial \mathrm{S_m}}{\partial \mathrm{T}}\right)_{\mathrm{V(m)}} \mathrm{dT} + \left(\frac{\partial \mathrm{S_m}}{\partial \mathrm{V_m}}\right)_{\mathrm{T}} \mathrm{dVV_m}$$

Comparison of equations (n) and (p) reveals the following relation.

$$\left(\frac{\partial S_m}{\partial V_m}\right)_T = \frac{p}{T}$$

Hence using equation h),

$$\left(\frac{\partial S_m}{\partial V_m}\right)_T = \frac{R}{V_m}$$

Thus at constant temperature,

$$\mathrm{dS_m = T\,d\ln(V_m)}$$

Hence the change in entropy for the isothermal expansion of an ideal gas between states where the volumes are $\mathrm{V_m(B)}$ and $\mathrm{V_m(A)}$ is given by equation (t).

$$S_m(B) - S_m(A) = R\,\ln\left[\frac{V_m(B)}{V_m(A)}\right]$$

We turn now to a consideration of changes in entropy from a statistical point of view.

A given experiment [8] uses two glass flasks of equal volumes connected by a glass tube which includes a tap, all at the same temperature T. The system contains N gas molecules; e.g. oxygen. The gas molecules pass freely between the two flasks through the open tap. On examining the contents of the two flasks we would not be surprised to discover that there are equal numbers of the gas molecules in the two flasks. The probability of this results from experiment A is expressed by stating that $\mathrm{P_y^A}$ is unity.

We return to the two flasks and close the tap. The probability that all the oxygen molecules are to be found in one flask is $(1/2)^{\mathrm{N}}$; i.e. a very low probability. If the total system contained only 20 molecules this probability signals a chance of 1 in 2^{20}. Thus the probability $\mathrm{P_y^B}$ for experiment B is very small; effectively zero.

An interesting exercise characterises these probabilities by a property σ. Then,

$$\sigma = \frac{R}{N}\ln(P_Y)$$

Note that the auxiliary property σ is generally negative because statistical probabilities vary between zero and unity. For the two experiments,

$$\sigma_B - \sigma_A = \frac{R}{N}\ln\left(\frac{P_Y^B}{P_Y^A}\right)$$

Hence,

$$\sigma_B - \sigma_A = \frac{R}{N}\ln\left(\frac{(1/2)^N}{1}\right)$$

Or,

$$\mathrm{\sigma_B - \sigma_A = -R\,\ln(2)}$$

We can express this result in general terms describing the expansions of one mole of gas from volume $\mathrm{V_A}$ to $\mathrm{V_B}$. Then,

$$\sigma_B - \sigma_A = R\,\ln[V_m(B)/V_m(A)]$$

At this point comparison between equations (t) and (y) is rewarding. Thus we may write the following equation.

$$\mathrm{S_m(B) - S_m(A) = \frac{R}{N}\left[\ln\left(P_Y^B\right) - \ln\left(P_Y^{\wedge}\right)\right]}$$

In other words the difference between the entropies in the ideal gas state is related to a probability. Thus we might conclude that $\mathrm{S_m(B)}$ is larger that $\mathrm{S_m(A)}$ because there are more ways of arranging molecules in system B than in system A. The state with the more ordered arrangement is the state with the lower entropy. It is a small step (but a very dangerous step) to draw comparison between entropy and (if there is such a word) the muddled-up-ness of a given system. But these are treacherous waters and outside the province of the classic thermodynamics which form the basis of the Topics. Indeed strong feelings are aroused. McGlashan [9,10], for example, takes to task chemists who assume that an increase in entropy implies an increase of disorder or of randomness or of 'mixed-upness'. We leave the debate here except to note that both authors of these Topics favour the view advanced by McGlashan [9,10] although this view would not a win a popularity contest. But 'popularity' is not an acceptable criterion in thermodynamics.

Footnotes

[1] Cambridge International Dictionary of English, Cambridge University Press, Cambridge, 1995.

[2] P. W. Atkins, Concepts in Physical Chemistry, Oxford University Press, Oxford, 1995.

[3] E. F. Caldin, An Introduction to Chemical Thermodynamics, Oxford University Press, Oxford, 1958.

[4] S. Glasstone, Sourcebook of Atomic Energy, MacMillan, London, 1954.

[5] P. W. Atkins and L. Jones, Chemistry: Molecules, Matter and Change, W H Freeman, New York, 3rd edition, 1997, p.875.

[6] Th. de Donder, Bull. Acad. Roy. Belg. (Cl.Sc), 1922, 7, 197, 205.

[7] I. Prigogine and R. Defay, Chemical Thermodynamics, transl. D. H. Everett, Longmans Green, London, 1954, (a) chapter 3; (b) chapter 4.

[8] G. N. Lewis and M. Randall, Thermodynamics , McGraw-Hill, New York, 1923, chapter VI.

[9] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979,pages 112-113;

[10] M.L. McGlashan, J. Chem. Educ.,1966,**43**,226.

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1.14.18: Electrochemical Units

Electric Current

The SI base electrical unit is the AMPERE which is that constant electric current which if maintained in two straight parallel conductors of infinite length and of negligible circular cross section and placed a metre apart in a vacuum would produce between these conductors a force equal to 2×10^{-7} newton per metre length. It is interesting to note that definition of the Ampere involves a derived SI unit, the newton. Except in certain specialised applications, electric currents of the order 'amperes' are rare. Starter motors in cars require for a short time a current of several amperes.

When a current of one ampere passes through a wire about 6.2×10^{18} electrons pass a given point in one second [1,2].

The coulomb (symbol C) is the electric charge which passes through an electrical conductor when an electric current of one A flows for one second. Thus

$$[\mathrm{C}] = [\mathrm{As}]$$

Electric Potential

In order to pass an electric current thorough an electrical conductor a difference in electric potential must exist across the electrical conductor. If the energy expended by a flow of one ampere for one second equals one Joule the electric potential difference across the electrical conductor is one volt [3].

Electrical Resistance and Conductance

If the electric potential difference across an electrical conductor is one volt when the electrical current is one ampere, the electrical resistance is one ohm, symbol Ω [4]. The inverse of electrical resistance , the conductance, is measured using the unit siemens, symbol [S]. [4]

Ohm's Law

This famous phenomenological law describes the ability of a system to conduct electrical charge. This law describes the relationship between three properties of an electrical conductor; e.g. a salt solution. The three properties are

i. electric current I described using the SI unit , ampere, symbol A;
ii. electric potential difference V across the electrical conductor using the SI unit , volt, symbol V; and
iii.

Ohm's Law is a phenomenological law in that it describes the phenomenon of electrical conductivity. Unlike the laws of thermodynamics, there are exceptions to Ohm's law for very high voltages and high frequency alternating electric currents. The (electrical) conductance G of a system is given by the inverse of its resistance R. The conductivity κ ($\equiv \sigma$) of a system is given by equation (c) [5].

$$\mathrm{j} = \kappa \mathrm{E}$$

Here j is the electric current density and E is the electric field strength. Chemists prefer to think in terms the charge carrying properties of a given system; i.e. the conductance G ($= 1/\mathrm{R}$) using the unit siemens, symbol S [5].

An interesting contrast often emerges between chemists and physicists, the latter seem to emphasise the property of 'resistance' whereas chemists are more interested in how systems transport electrical charge. Certainly the classic subject in chemistry concerns the electrical conductivities of salt solutions where the charge carriers are ions. The subject is complicated by the fact that there are two types of charge carriers in a given solution, cations and anions. Moreover the subject is further complicated by the fact that these charge carriers move in opposite directions with different velocities. In a solution containing a single salt the fraction of electric current carried by the cations and anions are called transport numbers; i.e. t_+ and t_- respectively for cations and anions where $\mathrm{t}_+ + \mathrm{t}_- = 1$.

Ionic Mobility

A given aqueous salt solution, volume V, is prepared using n_1 moles of water and n_j moles of a salt j. A pair of electrodes is placed in the solution, d metres apart. An electric potential, V volts, is applied across the solution and an electric current I is recorded. An electric charge Q coulombs ([As]) is passed through the solution. The electric current (unit [A]) is the rate of transport of charge, dQ/dt.

The speed of ion i through the solution v_i is given by the ratio of the distance travelled to the time taken. Thus v_i is a measure of the distance travelled in one second; $v = (a/t)\ [ms^{-1}]$. A more interesting property is the velocity of ion i in an electric field gradient measured using the ratio, volt/metre (Or, V/m). Thus electric mobility u_i has the unit, $[ms^{-1}/Vmm^{-1}] = [v_i E^{-1}] = [m^2\ s^{-1}\ V^{-1}]$.

The molar conductivity Λ of a salt solution is given by the ratio, $(\kappa/c_j)\ \{= [S\ m^2\ mol^{-1}]\}$. In fact the majority of research publications describe the dependence of Λ on the concentration of salt in a specified solvent at defined T and p. For salt solutions both cations and anions contribute to Λ; the transport number of an ion j describes the fraction of current carried by the j ion. Thus $t_j = |z_j|\ c_j\ v_j / \sum |z_i|\ c_i\ v_i$.

An electric current (i.e. a flow of electric charge) through a system is impeded by the electrical resistance. The ohm (symbol Ω) is the unit of electrical resistance being the ratio of electric potential (unit = volt) to electric current (unit = ampere) Then, ohm = volt/ampere (d)

In other words, Electrical resistance/ohm=[electric potential gradient /volt]/[electric current/ampere] . From equation (c) ohm (symbol Ω)

$$= VA^{-1} = m^2\ kg\ s^{-3}\ A^{-2}$$

The property (electrical) resistance is a measure of the impedance to the flow of electric charge. This somewhat negative outlook is not consistent with the attitude of chemists who are interested in the 'mechanism' by which a system **conducts** electrical charge. Chemists prefer to discuss the property of electric conductance rather than resistance. The conductance is measured using the unit siemen, symbol S [6]. A key component of electrical circuits is the electrical capacitance measured using the unit farad, symbol F [7].

If the composition of an electrical conductor is uniform, the electrical resistance is directly proportional to its length ℓ and inversely proportional to its cross sectional area, a. The material forming the conductor is characterized by its resistivity, ρ. Thus[8] resistance,

$$R = \rho\, \ell / a$$

Footnotes

[1] The electric charge on an electron $= 1.602 \times 10^{-19} C = 1.602 \times 10^{-19}$ As. A given single wire carries a current of 1 ampere.
Then in one second, the electric charge carried by that wire $= 1.602 \times 10^{-19}$ C
For one coulomb to pass a given point, the number of electrons passing $= \frac{1}{1.602 \times 10^{-19}}$
In other words 6.24×10^{18} electrons pass by.

[2] P.W. Atkins and L. Jones, Chemistry; Molecules, Matter and Change, W. H. Freeman, New York, 1997,p.658.

[3] $[V] \equiv \left[kgm^2\ s^{-3}\ A^{-1}\right] = \left[JA^{-1}\ s^{-1}\right]$

[4] $[\Omega] = \left[VA^{-1}\right] = \left[S^{-1}\right]$

[5] $\kappa = \left[Sm^{-1}\right]$
$\left[Am^{-2}\right] = \kappa\ \left[Vm^{-1}\right]$

[6] $S = \Omega^{-1}$

[7] $F = A^2\ s^4\ kg^{-1}\ m^{-2} = AsV^{-1} = CV^{-1}$

[8] $[S] \equiv \left[\Omega^{-1}\right] \equiv \left[AV^{-1}\right] \equiv \left[m^{-2}\ kg^{-1}\ s^3\ A^2\right]$
$[\Omega] = [\Omega m]\,[m]\,[m]^{-2}$

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1.14.19: Electrical Units

In attempting to understand the properties of chemical substances, chemists divide chemistry into two parts. In one part, chemists are interested in understanding **intramolecular** forces which hold molecules together. For example, using quantum mechanics and associated theories of covalent bonding, chemists describe the cohesive forces holding carbon, hydrogen and nitrogen atoms together in cyanomethane, $\mathrm{CH_3CN}$. At ambient temperature and pressure, cyanomethane is a liquid. In the second part of the sub-division of chemistry, chemists describe the intermolecular forces [1] which hold assemblies of molecules together in, for example, liquid and solid states; e.g. those forces which hold $\mathrm{CH_3CN}$ molecules together in the liquid state. Common experience tells us that intermolecular forces are weaker than intramolecular forces. When we heat $\mathrm{CH_3CN}(\ell)$ at ambient pressure, the liquid boils at a characteristic temperature to form a vapour. The intermolecular separation dramatically increases but the covalent bonds within $\mathrm{CH_3CN}$ do not break. [Of course, these bonds break at very high temperatures - thermolysis.] Here the emphasis centres on intermolecular cohesion. But this cannot be the whole story. If cohesion is the only force operating, molecules would collapse into each other in some nuclear catastrophe. This does not happen. Opposing the forces of cohesion are repulsive forces. In fact everyday experience leads to the idea of "size"; 'size is repulsive'.

Basic Physics

Molecules contain charged particles; protons (with positive electric charge) and electrons (with negative electric charge-- by convention). Intermolecular forces are understandable in terms of equations describing electrical interactions between electrically charged particles. An SI base unit is the ampere; symbol = A [2].

The SI unit of electric charge is the coulomb (symbol = \(\mathrm{C}) defined as \(\mathrm{A\,s}\) [3].

Electric Current

An electric current I is driven through an electrical resistance R, by an electric potential gradient across the resistance. An ammeter measures the electric current I. The voltmeter records the electric potential gradient, $\Delta\mathrm{E}$ across the resistance. The property called resistance R is given by Ohm's Law;

$$\Delta\mathrm{E} = \mathrm{I\,R}$$

In the IUPAC system the unit of resistance is ohm [symbol $\Omega \equiv \mathrm{VA^{-1}}$]. The electric potential difference is measured in volts, symbol V [4].

Electrical Capacitance

In a simple electric circuit, a small battery is connected across a parallel plate capacitance. No current flows in this circuit. The battery produces a set **of equal in magnitude but opposite in sign electric charges** on the two plates. A capacitance stores electric charge. In practice the extent to which a capacitance stores charge depends on the chemical substance between the two plates. This substance is characterised by its electric permittivity; symbol = ε. Where a vacuum exists between the two plates, the electric permittivity equals ε_0[5].

The permittivity of a liquid is measured by comparing capacitance C when the gap between the plates is filled with this liquid and with capacitance $\mathrm{C_0}$ when the gap is "in vacuo". Then

$$\varepsilon_\mathrm{r} = \varepsilon/\varepsilon_0 = \mathrm{C/C_0}$$

or

$$\mathrm{C} = \varepsilon_\mathrm{r}\,\mathrm{C_o}$$

For all substances, ε_r is greater than unity. In other words, with increase in ε_r so the electrical insulating properties of the system increase. At this stage, we have not offered a molecular explanation of the properly called ε_r but we have indicated that ε_r be can measured [6,7].

Intermolecular Forces and Energies

Molecule i and molecule j are separated by a distance r; we assert that r >> molecular radii of molecules i and j. Our discussion centres on the assertion that a force (symbol X) exists between the two molecules. Moreover, this force depends on the distance of separation r. Thus

$$X = f(r)$$

Ion-Interactions

The force X between two electric charges q_1 and q_2 distance r apart 'in vacuo' is given by equation (e); (Couloumb's Law) [8].

$$\mathrm{X} = \mathrm{q_1\, q_2}/4\,\pi\,\varepsilon_0\,\mathrm{r}^2$$

Two ions, i and j, have charge numbers z_i and z_j respectively [for K^+, $z_j = +1$; for SO_4^{2-}, $z_j = -2$]. For two ions 'in vacuo', the interionic force is given by equation (f).

$$\mathrm{F_{ij}} = (\mathrm{z_i e})\ (\mathrm{z_j e})\,/4\pi\,\varepsilon_0\,\mathrm{r}^2$$

But pairwise potential energy,

$$\mathrm{U}_{ij} = -\int_{\mathrm{ij}=\infty}^{\mathrm{r}} \mathrm{F_{ij}}\,\mathrm{dr}$$

Hence,

$$U_{ij} = (z_i e)\ (z_j e)\,/4\pi\,\varepsilon_0\,r$$

Equation (h) yields the interaction potential energy between a pair of ions [9]. The result is an energy expressed in joules. However, there are often advantages in considering an Avogadro number (i.e. a mole) of such pairwise interactions.

$$\mathrm{U_{ij}/Jmolmol_A^{-1}} = \mathrm{N_i e)}\ (\mathrm{z_j e})\,/4\pi\,\varepsilon_0\,\mathrm{r}$$

We consider two classes of ion-ion interactions:

i. Ions i and j have the same sign
   For cation-cation and anion-anion pairwise interactions the force between the ions is repulsive. The pairwise potential energy increases with decrease in ion-ion separation. To bring two ions having the same charge closer together we have to do work on the system, increasing the pairwise potential energy U_{ij}.
ii. Ions i and j have opposite signs
   For this system, $(z_i\, Z_j) < 0$. Ion-ion interaction is attractive and the potential energy U_{ij} decreases with decrease in r_{ij}. We write $|z_i\, z_j|$ to indicate the modulus of the product of the charge numbers.

$$\mathrm{U_{ij}/Jmol^{-1}} = -\mathrm{N_A}\ |\mathrm{Z_i\, Z_j}|\,\mathrm{e}^2/4\pi\,\varepsilon_0\,\mathrm{r}$$

Hence U_{ij} has a $(1/\mathrm{r})$ dependence on distance apart.

Electric field strength, E is the force exerted on unit charge at the point in question [10]. At distance r from charge q,

$$\mathrm{E} = \mathrm{q}/4\pi\,\varepsilon_0\,\mathrm{r}^2$$

Solvent Effects

An important topic in Chemistry concerns the effect of solvents on ion-ion interactions. Here we assume that solvents are characterised by their relative permittivities, ε_r. In a solvent the pairwise cation-anion interaction energy is given by equation (l).

$$\mathrm{U_{ij}/J} = -\,|\mathrm{z_i\, z_j}|\,\mathrm{e}^2/4\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{r}$$

$$\mathrm{U_{ij}/Jmolm^{-1}} = -\,|\mathrm{z_i\, Z_j}|\ \mathrm{N_A}\,\mathrm{e}^2/4\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\mathrm{r}$$

As commented above, ε_r is always greater than unity. Hence for a given system at fixed distance apart r, U_{ij} increases (becomes less negative) with increase in ε_r. With increase in ε_r, the ions are increasingly insulated and so at given distance r the stabilisation of the cation-anion pair is less marked.

Molecular Dipole Moments

A given molecule comprises an assembly of positive and negative charges. Consider a point 0, distance r from this assembly. We are concerned with the electric field strength at point 0, a short distance from the dipole moment. In the previous section we assumed that this assembly is simply characterised by the electric charge (i.e. $z_j\ e$ for ion j). However, in those cases where the overall charge is zero, a measurable electric field is detected at point 0. In 1912 Peter Debye showed that this field could be accounted for as a first approximation by characterising a molecule by its **dipole moment**. In the next approximation the electric field at 0 can also be accounted by an additional contribution from a distribution of charges within a molecule called a **quadrupole**, and in the next approximation by an additional contribution from a distribution called an **octupole** [11].

In a homonuclear diatomic molecule such as $\mathrm{H_2}$ and $\mathrm{Cl_2}$, the positive nuclei are embedded in charge clouds describing the distribution of negatively charged electrons. For such molecules the "centres" of positive charges and negative charges coincide. But for the molecule HCl the electron distribution favours the more electronegative chlorine atom. Hence the centres of positive and negative charges, magnitude $+\mathrm{q}$ and $-\mathrm{q}$, are separated by a dipole length ℓ. The molecule has a **dipole moment**, a characteristic and permanent property of an HCl molecule. The (molecular) dipole moment μ is given by the product '$\mathrm{q}\,\ell$'. A dipole moment has both magnitude and direction; it is a vector [12].

Footnotes

[1] The classic reference in this subject is: J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York 1954; corrected printing ,1964.

[2] The ampere is that constant current flowing in two parallel straight conductors, having negligible cross section, one metre apart in vacuo which produces a force between each metre of length equal to $2\time10^{-7}\ \mathrm{N}$.

[3] When a current of one A flows for one second, the total charge passed is one coulomb. In practice, a current of $1\ \mathrm{A}$ is very high and the common unit is milliampere (symbol: mA). The starter motor in a conventional car requires a peak current of around $30\ \mathrm{A}$.
Electric charge on a single proton, $\mathrm{e} = 1.602 \times 10^{-19}\mathrm{C}$.
Faraday, $\mathrm{F} = \mathrm{N_A\,e} = 9.649 \times 10^{4}\mathrm{Cmol}^{-1}$

[4] Just to keep up with the way the units are developing we note: - electric current coulomb $\mathrm{C} = \mathrm{A\ s}$ electric potential gradient volt $\mathrm{V} = \mathrm{JA}^{-1}\ \mathrm{s}^{-1} = \mathrm{JC}^{-1}$ (J = joule). Thus volt expressed as JC^{-1} is energy per coulomb of electric charge passed. This link between electric potential and energy is crucial. electrical resistance ohm $\Omega = \mathrm{VA}^{-1}$ Ohm's Law is a phenomenological law.

[5] Continuing our concern for units. electrical capacitance: unit = farad $\mathrm{F} \equiv \mathrm{AsV}^{-1}$ electric permittivity ε; unit = Fm^{-1} electric permittivity of a vacuum, $\varepsilon_0\ = 8.854\ \times 10^{-12}\ \mathrm{F\ m}^{-1}$ relative permittivity $\varepsilon_\mathrm{r}\ = \varepsilon/\varepsilon_0$; unit $\ = 1$ Older literature calls \(\epsilon_{\mathrm{r}}\), the "dielectric constant". But this property is not a constant for a given substance such as water (ℓ). Thus ε and ε_r depend on both temperature and pressure [6]; ε and ε_r for a given liquid depend on electric field strength and frequency of AC current applied to the capacitance.

[7] The quantity $\left(4\,\pi\,\varepsilon_0\,10^{-7}\right)^{-1/2}$ equals $2.998 \times 10^{8}\mathrm{ms}^{-1}$ which is the speed of light.

[8] We check the units. If X is a force, the unit for X is newton (symbol N). Then the right-hand side should simplify to the same unit. Electric charge is expressed in C[= As]; ε_0 has units of Fm^{-1} [= $\mathrm{AsV}^{-1}\ \mathrm{m}^{-1}$]. Then X = [C] [C]/[1] [1] $\left[\mathrm{AsV}^{-1}\ \mathrm{m}^{-1}\right]$ $[\mathrm{m}]^2$ But [V] = $\left[\mathrm{JA}^{-1}\ \mathrm{s}^{-1}\right]$ Then X = $\left[\mathrm{A}^2\ \mathrm{s}^2\right]$ / [AsJ^{-1} A s m] = [Jm^{-1}l = [N]

[9] We check that our units are correct. If U_{ij} is an energy expressed in joules, the terms on the right-hand side should reduce to joules. $\mathrm{U_{ij}} = [\mathrm{As}]\,[\mathrm{As}]/[1]\,[1]\ \left[\mathrm{AsV}^{-1}\ \mathrm{m}^{-1}\right]\ [\mathrm{m}] = \left[\mathrm{A}^2\ \mathrm{s}^2\right] / [\mathrm{AsJ}^{-1}\mathrm{As}] = [\mathrm{J}]$

[10]

$$\begin{aligned}\mathrm{E} &= [\mathrm{C}]/[1]\,[1]\ \left[\mathrm{AsV}^{-1}\ \mathrm{m}^{-1}\right]\ \left[\mathrm{m}^2\right] \\ &= [\mathrm{As}]/[\mathrm{AsVm}] = \left[\mathrm{Vm}^{-1}\right] \\ &= \left[\mathrm{JA}^{-1}\ \mathrm{s}^{-1}\ \mathrm{m}^{-1}\right] = \left[\mathrm{Jm}^{-1}\right]/[\mathrm{As}] = \left[\mathrm{NC}^{-1}\right]\end{aligned}$$

Thus electric field strength is expressed in Vm^{-1} or NC^{-1}; the latter is clearly a force per unit charge.

[11] The classic text is:- P. Debye, Polar Molecules, Chemical Catalog Co., New York 1929 (available as Dover paperback). We do not consider here interactions involving quadrupoles, octupoles, etc. These molecular properties are reviewed by A. D.

Buckingham, Quart. Rev., 1959, **13**, 183.

[12] Dipole moment, $\mu = \mathrm{q}\,\ell = [\mathrm{C}]\ [\mathrm{m}]$ Thus $\mu = [\mathrm{Cm}]$, coulomb metre . Dipole moments are normally quoted using the unit, debye. [The unit is named in honour of Peter Debye.] $1\mathrm{D} = 3.336 \times 10^{-30}\mathrm{Cm}$.

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1.14.20: Electric Conductivities of Salt Solutions- Dependence on Composition

At temperature T and pressure p, the molar conductivity of given salt solution Λ depends on the concentration of salts. This subject has an extensive scientific literature. One of the challenges is to calculate Λ for given salt solution knowing the properties of the pure solvent and the salt at specified T and p. A key quantity is the limiting molar conductivity Λ^{∞} defined for a given salt solution by equation (a).

$$\mathrm{Lt}\,(c_j \rightarrow 0)\,\Lambda = \Lambda^{\infty}$$

Moreover as Kohlrausch showed in 1876 (> 125 years ago) a given Λ^{∞} can be expressed as the sum of limiting molar ionic conductances, $\lambda_{\mathrm{j}}^{\infty}$. Thus

$$\Lambda^{\infty} = \sum_{j=1}^{j=i} \lambda_j^{\infty}$$

A difficult theoretical task is to estimate $\lambda_{\mathrm{j}}^{\infty}$ for a given ion at defined T and p and specified solvent. Rather more progress has been made in predicting quantitatively the dependence of $(\Lambda - \Lambda^{\infty})$ on concentration of salt in a given solvent at defined T and p assuming that the ions in solution are characterised by their electric charges and radii. Indeed quantitative treatments of the electrical conductivities of salt solutions have attracted enormous interest and provided a challenge to scientists with good mathematical abilities. Here we summarise briefly the essence of treatments published by Onsager [1-3] and by Fuoss [3,4]. The account given below is based on that set out by N. K. Adam [5].

A relaxation effect and an electrophoretic effect contribute to the magnitude of $(\Lambda - \Lambda^{\infty})$ for a real salt solution for which $\Lambda < \Lambda^{\infty}$. In a real solution under the influence of an applied electric field, anions and cations move in opposite direction. The word ‘move’ does not reflect the complexity of the real situation. In a real solution and in the absence of an applied electric field, the ions move in random directions, Brownian motion, as a consequence of the thermal energy of the system. In some sense, ions and solvent molecules are jostling continuously. When an electric potential gradient is applied across the solution, the previously random motion of ions is now biased in a particular direction depending on the ionic charge. If the solution is ‘infinitely dilute’, the velocity of a given ion is characteristic of the ion, solvent, temperature and pressure.

In a real solution the mobility decreases with increase in concentration of salt. Two retarding effects are identified, relaxation and electrophoretic effects. The latter emerges from the fact that a given j ion moves against the flow of counter-ions together with associated solvent molecules. In a real solution and in the absence of an applied electric field, a given j ion is at the centre of an ion atmosphere which has an electric charge equal in magnitude but opposite in sign to that of the j ion. Under the impact of an applied electric field the j-ion moves away from the centre of the ion atmosphere. The latter pulls the j-ion back towards this centre. In other words the j-ion is retarded by this relaxation effect. The latter term reflects the fact that the retardation depends on the rate at which the electric charge density in the ion atmosphere grows as the j ion moves through the solution and decays in the wake of the j ion.

Ionic Mobility

A given salt solution at temperature T and pressure p contains a sa }\)]. In solution, the motion of ions is quite random, a pattern usually described as Brownian motion. If however an electric field is applied across the solution the movement of ions is biased in a given direction depending on the sign of the charge on the j ion. The electrical mobility u_j of ion j describes the velocity of ion-j in an electric field gradient measured in $[\mathrm{Vm}^{-1}]$ [6]. In the absence of ion-ion charge-charge interaction , the electrical mobility $\mathbf{u}_j^{\infty}$ is characteristic of the j ion, solvent, temperature and pressure. The superscript ‘∞’ identifies that to all intents and purposes the j ion is in an infinitely dilute solution. However in a real solution, concentration c_i in salt i, the j ion is surrounded by an ‘ion atmosphere’ which has an electric charge equal in magnitude but opposite in sign to that on the j ion.

Electrophoretic Effect

The ion atmosphere is modelled as a series of shells, thickness dr distance r from the centre of the j ion. The electrical charge q_j on a shell distance r from the j ion is given by equation (c) [7].

$$q_j = 4\,\pi\,r^2\,\rho\,dr$$

Here ρ is the electric charge density, measured in 'coulombs per cubic metre'. As a result of the electric field gradient operating on the j ion the electric force F expressed in newtons operating on this shell [8] is given by equation (d).

$$\mathrm{F} = 4\,\pi\,\mathrm{r}^2\,\rho\,\mathrm{E}\,\mathrm{dr}$$

According to Stokes Law, a sphere having radius r and moving with velocity v through a liquid having (shear) viscosity η is subject to a viscous resistance R_η, a force expressed in newtons and given by equation (e) [9].

$$\mathrm{R}_\eta = 6\,\pi\,\eta\,\mathrm{r}\,\mathrm{V}$$

If the speed of the liquid stream increases by dv when the radius of the shell defining the ion atmosphere increases by dr, the viscous resistance increases by $(6\,\pi\,\eta\,r\,dv)$. If the motion of the j ion through the solution is steady, the increase in viscous resistance to movement of the j ion equals the electrical force (see equation d). Therefore

$$6\,\pi\,\eta\,r\,dv = 4\,\pi\,r^2\,\rho_j\,E\,dr$$

The charge density ρ_j is obtained by combining equations (u) and (x) of Topic 680. Thus [10],

$$\rho_\mathrm{j} = -\frac{(\mathrm{z_j\,e})\,\exp\,(\kappa\,\mathrm{a_j})}{4\,\pi\,\varepsilon_0\,\varepsilon_\mathrm{r}\,)\,1+\kappa\,\mathrm{a_j})}\,\varepsilon_0\,\varepsilon_\mathrm{r}\,\kappa^2\,\frac{\exp(-\kappa\,\mathrm{r})}{\mathrm{r}}$$

Then with $\ell^{-1} = \kappa$,

$$p_j = -\frac{z_j\,e\,\exp\,(a_j/\ell)\,\exp(-r/\ell)}{4\,\pi\,\ell\,\,(a_j+\ell)\,\,r}$$

From equation (f),

$$\mathrm{dv} = \frac{2}{3}\,\frac{\rho_\mathrm{j}}{\eta}\,\mathrm{E}\,\mathrm{r}\,\mathrm{dr}$$

Hence

$$\mathrm{dv} = -\frac{2\,\mathrm{z_j\,e}\,\exp\,(\mathrm{a_j}/\ell)}{12\,\pi\,\eta\,\ell\,\,(\mathrm{a_j}+\ell)}\,\mathrm{E}\,\exp(-\mathrm{r}/\ell)\,\mathrm{dr}$$

Equation (j) is integrated between limits (i) $r = \sigma$ to $r = \infty$, and (ii) $v = 0$ and v_1 where v_1 is the stream velocity of the solution outside the ion atmosphere of the j ion. Then

$$\mathrm{v_1} = \frac{\mathrm{z_j\,e\,E}\,\exp\,(\mathrm{a_j}/\ell)}{6\,\pi\,\eta\,\ell\,\,(\mathrm{a_j}+\ell)}\,\int_{\mathrm{a_j}}^{\infty}\exp(-\mathrm{r}/\ell)\,\mathrm{dv}$$

Hence,

$$\mathrm{v_1} = -\frac{\mathrm{z_j\,e\,E}}{6\,\pi\,\eta\,\,(\mathrm{a_j}+\ell)}$$

For dilute solutions, $\mathrm{a_j} << \ell$ such that the stream velocity of the solution outside the ion atmosphere is given by equation (m)

Therefore [11]

$$\mathrm{v_1} = -\frac{\mathrm{z_j\,e\,E}}{6\,\pi\,\eta\,\ell}$$

We shift the reference. The solvent does not physically move when we measure the electrical conductivity of a solution. Therefore the impact of the electrophoretic effect is to retard the j-ion in solution. The decrease in electrical mobility of the j ion is given by equation (n) [12].

$$-\,(\Delta\mathrm{u_j})_{\mathrm{electrpbor}} = -\frac{\mathrm{z_j\,e}}{6\,\pi\,\eta\,\ell}$$

Relaxation Effect

In the limit of infinite dilution, a given j-ion proceeds through an aqueous solutions at defined T and p under the influence of an applied electric field gradient. The impediment to its progress arises from the solvent molecules. However in a real salt solution, the j ion is surrounded by its ion atmosphere which has an electric charge equal in magnitude and opposite on sign. In the absence of an applied electric field the ion atmosphere is spherically symmetric about the j ion. In a real solution, the migrating ion is not at the centre of the ion atmosphere, the latter therefore retarding the migrating ion. This retardation is called the relaxation effect on the grounds that the build-up of the ion atmosphere preceeding the ion and the decay in the wake of the ion is characterised by a relaxation time.

The relaxation effect can be understood in terms of irreversible thermodynamics. Thus the flow of cations and anions in opposite directions are coupled. The stronger the coupling the greater is the retardation of the migrating ions. The first treatment of this coupling of flows and forces was developed by Onsager who published a reasonably successful description of the impact of this coupling on ionic mobilities. The analogue of equation (n) describing the relaxation effect takes the following form [13] where w is a correction factor depending on the type of electrolyte [14].

$$-(\Delta u_j) = \frac{e^3\, w\, u_j^{\infty}}{24\, \varepsilon^0\, \varepsilon_{\mathrm{r}}\, k\, T\, \ell}$$

Here ℓ is the radius of the ion atmosphere surrounding the j ion ; equation (p) where the concentration of j ions c_j is expressed in moldm^{-3}.

$$\ell = \frac{10^3\, 4\, \pi\, \varepsilon^0\, \varepsilon_{\mathrm{r}}\, \mathrm{k\,T}}{8\, \pi\, \mathrm{e}^2\, \mathrm{N_A\, I}}$$

For dilute solutions

$$I = (0.5) \sum_{i=1}^{i=j} c_i\, z_i^2$$

Molar Conductivity

In summary two retarding effects, electrophoretic and relaxation, mean that the molar conductivity of a given aqueous salt solution is less than the molar conductivity of the corresponding solution at infinite dilution, Λ^{∞}. The outcome is the famous Debye-Huckel-Onsager Equation for molar conductivities. For a 1:1 salt (e.g. KBr) in aqueous solution at $298.15\ \mathrm{K}$ and ambient pressure, the molar conductivity Λ is given by equation (r) [15,16].

$$\Lambda = \Lambda^{\infty} - (0.229\, \Lambda^{\infty} + 60.2)\ (c_j/c_r)^{1/2}$$

Footnotes

[1] L. Onsager, Physik. Z.,1926,**27**,388.

[2] L. Onsager, Trans. Faraday Soc.,1927,**23**,341.

[3] L. Onsager and R. M. Fuoss, J. Phys. Chem.,1932,36,2689.

[4] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 1950, 2nd edn. Revised and enlarged

[5] N. K. Adam, Physical Chemistry, Oxford, 1956.

[6]

$$v_j = \left[\mathrm{ms}^{-1}\right]$$
$$u_j = \left[\mathrm{ms}^{-1}\right] / [\mathrm{Vm}$$

[7] $\mathrm{q_j} = [1]\,[1]\ \left[\mathrm{m}^2\right]\ \left[\mathrm{Cm}^{-3}\right]\ [\mathrm{m}] = [\mathrm{C}]$

[8] $4\, \pi\, r^2\, \rho\, E\, dr = [1]\,[1]\ \left[\mathrm{m}^2\right]\ \left[\mathrm{Cm}^{-3}\right]\ \left[\mathrm{Vm}^{-1}\right]\ [\mathrm{m}] = \left[\mathrm{Jm}^{-1}\right] = [\mathrm{N}]$

[9] $\mathrm{R}_{\eta} = [1]\,[1]\ \left[\mathrm{kgm}^{-1}\ \mathrm{s}^{-1}\right]\ [\mathrm{m}]\ \left[\mathrm{ms}^{-1}\right] = \left[\mathrm{kgms}^{-22}\right] = [\mathrm{N}]$

[10] $\rho_j = \frac{[1]\,[\mathrm{C}]\,[1]}{[1]\,[1]\,[\mathrm{Fm^{-1}}]\,[1]\,[1]} \frac{[\mathrm{Fm^{-1}}]\,[1]\,[\mathrm{m}]^2\,[1]}{[\mathrm{m}]} = [\mathrm{Cm^{-3}}]$

[11] \(\mathrm{v}_{1}=\frac{[\mathrm{l}] \,[\mathrm{C}] \,\left[\mathrm{V} \mathrm{m} \mathrm{m}^{-1}\right]}{[\mathrm{l}] \,[\mathrm{l}] \,\left[\mathrm{kg} \mathrm{m}^{-1} \mathrm{~s}^{-1}\right] \,[\mathrm{m}]} \mathrm{v}_{1}=\frac{[\mathrm{l}] \,[\mathrm{C}] \,\left[\mathrm{V} \mathrm{m} \mathrm{m}^{-1}\right]}{[\mathrm{l}] \,[\mathrm{l}] \,\left[\mathrm{kg} \mathrm{m}^{-1} \mathrm{~s}^{-1}\right] \,[\mathrm{m}]}

[12] $\Delta \mathrm{u_j} = \frac{[\mathrm{ms^{-1}}]}{[\mathrm{Vm^{-1}}]} = [\mathrm{m^2\ V^{-1}\ s^{-1}}]$

$-\left(\Delta \mathrm{u_j}\right)_{\mathrm{relax}} = \frac{[\mathrm{A^2\ s^2}]}{[1]\,[\mathrm{Fm^{-1}}]\,[1]\,[\mathrm{JK^{-1}}]\,[\mathrm{K}]\,[\mathrm{m}]}\,\mathrm{u_j^\infty}$

[13] $= \frac{[\mathrm{A^2\ s^2}]}{[\mathrm{F}]\,[\mathrm{J}]} = \frac{[\mathrm{A^2\ s^2}]}{[\mathrm{A^2\ s^4\ kg^{-1}\ m^{-2}}]\,[\mathrm{kgmm^2\ s^{-2}}]}\,\mathrm{u_j^\infty}$

$= [1]\,\mathrm{u_j^\infty}$

[14] For an advanced treatment, see J. O'M. Bockris and A.K.N Reddy, Modern Electrochemistry: Ionics, Plenum Press, New York, 2nd. edn.,1998, chapter 4.

[15] P. W. Atkins, Physical Chemistry, Oxford University Press, 1982, 2nd. edn., p.900.

[16] $\Lambda = [\Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}]\,; 0.229 = [1]; 60.2 = [\Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}]$

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1.14.21: Donnan Membrane Equilibria

A given experimental system comprises two compartments, I and II, separated by a membrane. The two compartments contain aqueous solutions at common temperature and pressure. The experimental system is set up by placing in compartment I an aqueous salt solution; e.g. $\mathrm{NaCl(aq)}$ having concentration $\mathrm{c_1\ moldm^{-3}}$. However compartment II contains a salt, $\mathrm{R^+Cl^-(aq)}$, concentration $\mathrm{c_2\ moldm^{-3}}$. The membrane is permeable to both $\mathrm{Na^+}$*and*\($\mathrm{Cl^-}$ ions but not to $\mathrm{R^+}$ cations. The sodium and chloride ions spontaneously diffuse across the membrane until the two solutions are in thermodynamic equilibrium. We represent the equilibrium system as follows where | | represents the membrane.

[I]

$$\mathrm{Na^+\ (c_1-\alpha)^{cq}\ Cl^-\ (c_1-\alpha)^{eq}\ ||[II]Na^+(\alpha)^{eq}R^+\ (c_2)^{eq}\ Cl^-\ (c_2+\alpha)^{eq}}$$

The solutions on both sides are electrically neutral. A thermodynamic analysis is somewhat complicated if account is taken of the role of ion-ion interactions. However the essential features of the argument are revealed if we identify the activities of the ions as equal to their concentrations.

Hence at equilibrium at fixed T and p,

$$\begin{array}{l}\left[\mu^0\left(\mathrm{Na^+;aq}\right)+\mathrm{R\,T\ ln}\left\{(\mathrm{c_1}-\alpha)^{\mathrm{eq}}_{\mathrm{Na}}/\mathrm{c_r}\right\}\right]_{\mathrm{I}}\\ +\left[\mu^0\left(\mathrm{Cl^-;aq}\right)+\mathrm{R\,T\ ln}\left\{(\mathrm{c_1}-\alpha)^{\mathrm{eq}}_{\mathrm{Cl}}/\mathrm{c_r}\right\}\right]_{\mathrm{I}}=\\ \left[\mu^0\left(\mathrm{Na^+;aq}\right)+\mathrm{R\,T\ ln}\left\{\alpha^{\mathrm{eq}}_{\mathrm{Na+}}/\mathrm{c_r}\right\}\right]_{\mathrm{II}}\\ +\left[\mu^0\left(\mathrm{Cl^-;aq}\right)+\mathrm{R\,T\ ln}\left\{(\mathrm{c_2}+\alpha)^{\mathrm{eq}}_{\mathrm{Cl-}}/\mathrm{c_r}\right\}\right]_{\mathrm{II}}\end{array}$$

But

$$(c_1-\alpha)^{\mathrm{eq}}_{\mathrm{Na+}}=(\mathrm{c_1}-\alpha)^{\mathrm{eq}}_{\mathrm{Cl-}}$$

Or,

$$\left[(c_1-\alpha)^{\mathrm{eq}}_{\mathrm{Na+}}\right]^2=\alpha^{\mathrm{eq}}_{\mathrm{Na+}}\ (\mathrm{c_2}+\alpha)^{\mathrm{eq}}\,\mathrm{CI^-}$$

Then [1],

$$\frac{\alpha^{\mathrm{eq}}}{\mathrm{c_1}}=\frac{\mathrm{c_1}}{2\,\mathrm{c_1}+\mathrm{c_2}}$$

The latter is Donnan's Equation. The ratio $(\alpha^{\mathrm{eq}}/\mathrm{c_1})$ tends to be smaller the larger is $\mathrm{c_2}$. This conclusion is confirmed by experiment.

We have simplified the algebra by writing $\mathrm{R^+Cl^-}$ as the salt in compartment II. In practice the Donnan equilibrium finds major application where salt RCl is a macromolecule [2-4].

Footnotes

[1] $\mathrm{c_1^2-2\,\alpha\,c_1+\alpha^2=\alpha\,c_2+\alpha^2}$

Then, $c_1^2-2\,\alpha\,c_1=\alpha\,c_2$

Or, $\alpha=\frac{c_1^2}{2\,c_1+c_2}$

[2] F. G. Donnan et al, J. Chem. Soc.,1911, 1554; 1914,1941.

[3] F. G. Donnan, Chem. Rev.,1924, **1**,73.

[4] F. G. Donnan and E. A. Guggenheim, Z. Physik Chem. A, 1932,**162**,346.

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1.14.22: Descriptions of Systems

Important themes in thermodynamics involve (i) properties (variables) which can be measured (e.g. volumes and/or densities) and (ii) thermodynamic variables which are rigorously defined (e.g. enthalpies). In these terms a measured property (e.g. density) is the reporter of the chemical properties or processes taking place in a system. So it is always important to ask if the "reporter" can be interrogated for the required information. In fact there is often a limit to the amount of information which a given reporter offers to the investigator. These important limitations should be borne in mind. An example makes the point.

A system is prepared by placing $\mathrm{n}_{\mathrm{X}}^{0}$ moles of substance in a closed vessel at fixed T and p. [The superscript '0' implies at zero time.] We explore two possible descriptions of this system. Perhaps two samples were analysed by two independent laboratories.

Description A

The first laboratory reports that the system is simple and contains the single substance X.

Gibbs energy

$$\mathrm{G(A)} = \mathrm{n}_{\mathrm{X}}^{0}\,\mu_{\mathrm{X}}^{*}(\ell)$$

and volume

$$\mathrm{V(A)} = \mathrm{n}_{\mathrm{X}}^{0}\,\mathrm{V}_{\mathrm{X}}^{*}(\ell)$$

Here $\mu_{X}^{*}(\ell)$ and $\mathrm{V}_{\mathrm{x}}^{*}(\ell)$ are the chemical potential and molar volume of the pure chemical substance X.

Description B

The second laboratory identifies two substances X and Y in chemical equilibrium such that the equilibrium amounts of substances X and Y are respectively $\mathrm{n}_{\mathrm{X}}^{\mathrm{eq}}$ and $\mathrm{n}_{\mathrm{Y}}^{\mathrm{eq}}$.

Gibbs energy

$$\mathrm{G(B)} = \mathrm{n}_{\mathrm{X}}^{\mathrm{eq}}\,\mu_{\mathrm{X}}^{\mathrm{eq}} + \mathrm{n}_{\mathrm{Y}}^{\mathrm{eq}}\,\mu_{\mathrm{Y}}^{\mathrm{eq}}$$

and volume

$$\mathrm{V(B)} = \mathrm{n}_{\mathrm{X}}^{\mathrm{eq}}\,\mathrm{V}_{\mathrm{X}}^{\mathrm{eq}} + \mathrm{n}_{\mathrm{Y}}^{\mathrm{eq}}\,\mathrm{V}_{\mathrm{Y}}^{\mathrm{eq}}$$

Here $\mu_{\mathrm{X}}^{\mathrm{eq}}$ and $\mu_{\mathrm{Y}}^{\mathrm{eq}}$ are the equilibrium chemical potentials; $\mathrm{V}_{\mathrm{X}}^{\mathrm{eq}}$ and $\mathrm{V}_{\mathrm{Y}}^{\mathrm{eq}}$ are the equilibrium partial molar volumes.

Description A is "primitive" and Description B is "sophisticated". Both Gibbs energies and volumes are functions of state so that $\mathrm{V(A)} = \mathrm{V(B)}$ and $\mathrm{G(A)} = \mathrm{G(B)}$. The chemical potential of substance X describes the change in G when δn_{X} moles of X are added. This chemical potential is insensitive to the changes taking place in the equilibrium system;$\mu_{X}(\ \mathrm{A}) = \mu_{X}(\ \mathrm{B})$. Consequently, measurement of volume V [and if it were possible of G] would not distinguish between the two descriptions. Similarly, measurement of H (if it were possible) would not distinguish between the two descriptions.

Footnotes

[1] L. P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, 2nd edn., 1970,p.16.

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1.14.23: Enzyme-Substrate Interaction

We consider the formation in aqueous solution of an enzyme –substrate complex ES by an enzyme E and substrate S. The system is prepared using $\mathrm{n}^0(\mathrm{E})$ moles of enzyme and $\mathrm{n}^0(\mathrm{S})$ moles of substrate; equation (a)

	$\mathrm{E(aq)}+$	$\mathrm{S(aq)} \Leftrightarrow$	$\mathrm{ES(aq)}$
At $t = 0$	$\mathrm{n}^0(\mathrm{E})$	$\mathrm{n}^0(\mathrm{S})$	0 mol
At $t = \infty$	$n^0(E) - \xi$	$\mathrm{n}^0(\ \mathrm{S}) - \xi$	ξ mol

The upper limit of the extent of interaction ξ is controlled by whichever is the smallest amount, either $\mathrm{n}^0(\mathrm{E})$ or $\mathrm{n}^0(\mathrm{S})$. The latter two variables determine the total amount of $\mathrm{ES(aq)}$ which can be formed in the limit of tight binding.

The approach described above can be extended to more complicated schemes involving multip-step reactions. In the following we consider the case where enzyme E converts substrate A into product D. The system is prepared using $\mathrm{n}^0(\mathrm{E})$ moles of enzyme and $\mathrm{n}^0(\mathrm{A})$ moles of substrate A such that there are two intermediates $\mathrm{EB(aq)}$ and $\mathrm{EC(aq)}$, product D being liberated from the bound state in the final step. The equilibrium state can be represented by the following scheme.

$$\begin{array}{llllll} \mathrm{E(aq)} & +\mathrm{A(aq)} \Leftrightarrow \mathrm{EB(aq)} & \Leftrightarrow \mathrm{EC(aq)} & \Leftrightarrow \mathrm{E(aq)} + \mathrm{D(aq)} \\ \mathrm{n}^0(\mathrm{E}) - \xi_1 + \xi_3 & \mathrm{n}^0(\ \mathrm{A}) - \xi_1 & \xi_1 - \xi_2 & \xi_2 - \xi_3 & \mathrm{n}^0(\mathrm{E}) - \xi_1 + \xi_3 \xi_3 \end{array}$$

The key point is that at equilibrium the amounts of enzyme $\mathrm{E(aq)}$ identified at both ends of the reaction must be the same. Further a mass balance shows that the total amount of enzyme present equals $\mathrm{n}^0(\mathrm{E})$ mol. Other features are interesting; ξ_3 must be zero if ξ_2 is zero. The method can be applied to more complicated reaction schemes including those where the path from reactant to product involves parallel reactions.

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1.14.24: Equation of State- General Thermodynamics

We take up the challenge of seeking an equation of state for all chemical substances. We confine attention to closed systems containing one chemical substance. We also confine our attention to systems at equilibrium where the affinity for spontaneous change is zero. A calculus operation allows us to relate p, V and T.

$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1$$

By definition, the equilibrium isobaric expansivity. [1]

$$\alpha_p(A=0) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,A=0}$$

The equilibrium isothermal compressibility [2],

$$\kappa_{\mathrm{T}}(\mathrm{A}=0) = -\frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T,A=0}}$$

Hence,

$$\left(\frac{\partial p}{\partial T}\right)_{V,A=0} = \frac{\alpha_p(A=0)}{\kappa_T(A=0)}$$

$\left(\frac{\partial p}{\partial T}\right)_{V,A=0}$ is the equilibrium isochoric thermal pressure coefficient. [3] Equation (d) shows that this property can be obtained from the experimentally accessible, $\alpha_p(A=0)$ and $\kappa_{\mathrm{T}}(\mathrm{A}=0)$. In fact the coefficient can be directly measured, at least for liquids. [4] From the Master Equation where the affinity for spontaneous change is zero,

$$\mathrm{dU} = \mathrm{T\,dS} - \mathrm{p\,dV}$$

At constant T,

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} - \mathrm{p}$$

Using a Maxwell Equation,

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - \mathrm{p}$$

All terms on the right hand side of equation (g) are experimentally accessible. Moreover this equation applies to all systems, solids, liquids and gases. By definition,

$$\beta_{\mathrm{V}} = \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

Then,

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \mathrm{T}\,\beta_{\mathrm{V}} - \mathrm{p}$$

Equation (i) is a Thermodynamic Equation of State. Equation (j) is another Thermodynamic Equation of State. [5]

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \mathrm{V}\,(1 - \mathrm{T}\,\alpha_{\mathrm{p}})$$

For many condensed phases the product $\mathrm{T}\,\beta_{\mathrm{v}}$ is much larger than the pressure p. Hence

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \cong \mathrm{T}\,\beta_{\mathrm{V}}$$

The partial differential $\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$ is the internal pressure, π_j for liquid j. [6] Originally the term 'internal pressure' referred to the product , $\mathrm{T}\,\beta_{\mathrm{v}}$. The closely related ratio of molar thermodynamic energy of vaporisation to molar volume $\left[\frac{\Delta_{\mathrm{vap}}\mathrm{U}^0}{\mathrm{V}^*(\ell)}\right]$ is the cohesive energy density,

$$\text{c.e.d.} = \left[\frac{\Delta_{\text{vap}}\mathrm{U}^0}{\mathrm{V}^*(\ell)}\right]$$

The rational behind this definition notes that $\Delta_{\text{vap}}\,\mathrm{U}^0$ defines the change in thermodynamic energy when one mole of a given substance passes from the liquid to the vapour state, breaking strong cohesive forces in the liquid. By dividing by the molar volume of the liquid we normalise this change to a fixed volume. [7]

Internal pressures are interesting parameters. [8,9] Nevertheless despite their thermodynamic basis, treatments of chemical properties in terms of internal pressures receive only sporadic attention. One feels they should be more informative but it is not always clear how one draws conclusions from analysis of experimental data using these properties.

Footnotes

[1] $\alpha_p = \frac{1}{[m^3]}\frac{[\mathrm{m}^3]}{[\mathrm{K}]} = [\mathrm{K}^{-1}]$

[2] $\kappa_{\mathrm{T}} = \frac{1}{[\,\mathrm{m}^3]}\frac{[\mathrm{m}^3]}{[\mathrm{Nm}^{-3}]} = [\mathrm{Nm}^{-2}]^{-1} = [\mathrm{Pa}]^{-1}$

[3] $\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right) = \frac{[\mathrm{Nm}^{-2}]}{[\mathrm{K}]} = [\mathrm{PaK}^{-1}]$

[4] A small amount of liquid sample is held in a sample cell sealed by a piston; the latter is linked to a device which allows a known pressure to be applied to the sample. The sample cell is held in a thermostat; the temperature of the latter is tightly controlled. The temperature is changed by a small amount; $\Delta\mathrm{T}$. The volume of the liquid in the sample cell (normally) increases. The applied pressure is changed by a small amount $\Delta\mathrm{p}$ in order to recover the original volume. Then for a given liquid at defined p, V and T, we have the ratio $(\Delta\mathrm{p}/\Delta\mathrm{T})$.

[5] J. S. Rowlinson and F. L. Swinton, Liquids and Liquid Mixtures, Butterworths, London, 3rd. edn., 1982, p.12.

[6] $\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \frac{[\mathrm{J}]}{[\mathrm{m}^3]} = [\mathrm{Nm}^{-2}] = [\mathrm{Pa}]$

[7] Links between calorimetry and equations of state are discussed by S. L. Randzio, Chem. Soc. Rev., 1995, **24**, 359.

[8]

a. W. Westwater, H. W. Frantz and J. H. Hildebrand, Phys. Rev., 1928, **31**,135.
b. J. H. Hildebrand, Phys. Rev.,1929, **34**, 649, 984.
c. J. H. Hildebrand and R. H. Lamoreaux, Ind. Eng. Chem. Fundam., 1974, **13**, 110.
d. J. H. Hildebrand, Proc. Natl. Acad.Sci. USA, 1967, **57**, 542.

[9] $\mathrm{T/K} = 298.15$

Liquid \(\pi_{\mathrm{i}} /10^{8} \mathrm{Pa} \quad \mathrm{c.e.d}./10^{8} \mathrm{Pa}\)
Methanol 2.930 8.600
DMSO 5.166 7.047
Water 1.013 22.98

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1.14.25: Equation of State- Perfect Gas

A closed system contains n_j moles of a gaseous substance j. No chemical reaction takes place in the system. The system is at equilibrium where the affinity for spontaneous change is zero. The system is characterised by the thermodynamic energy U. The system is displaced to a neighbouring equilibrium state by a change in entropy dS and a change in volume dV. The change in thermodynamic energy is given by the Master Equation.

$$dU = T\,dS - p\,dV$$

At equilibrium the isothermal dependence of thermodynamic energy on volume is given by equation (b).

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

In attempting to understand from a chemical standpoint the properties of gases, liquid mixtures and solutions, a common approach formulates a set of properties which classify a given system as ideal. The definition of an ideal (or, perfect) system is made with practical chemistry in mind. When examining the properties of gases there is merit in identifying the properties of a perfect gas. [No real gas is perfect!] If the gaseous substance j is a perfect gas, the following conditions [1] are met at all temperatures and pressures.

A. $(\partial U/\partial V)_T = 0$
B. $p\,V = n_j\,R\,T$

Here R is the gas constant, $8.314\ J\ K^{-1}\ mol^{-1}$. Conditions (A) and (B) are equivalent [2]. In most cases condition (B) is quoted because the equation links three practical properties, p, V and T.

Footnotes

[1]

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{[J]}{[m^3]} = \frac{[Nm]}{[m^3]} = [Nm^2] = [Pa]$$
$$p\,V = [Nm^{-2}]\ [m^3] = [Nm] = [J]$$
$$n_j\,R\,T = [mol]\ [JK^{-1}\ mol^{-1}]\ [K] = [J]$$

[2] From definition (A) and equation (b),

$$p = T\left(\frac{\partial S}{\partial V}\right)_T$$

We use a Maxwell equation;

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Hence from equations (i) and (ii),

$$p = T\left(\frac{\partial p}{\partial T}\right)_v$$

From definition (B),

$$\left(\frac{\partial p}{\partial T}\right)_V = n_j\,R/V = p/T$$

Equations (iii) and (iv) are the same. Hence definition (B) is the integrated form of definition A. The gas constant R is experimentally determined.

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1.14.26: Equation of State - Real Gases, van der Waals, and Other Equations

The properties of gases pose a formidable challenge for chemists who seek to understand their $\mathrm{p-V-T}$ properties. Chemists adopt an approach which starts by defining the properties of a (hypothetical) ideal gas (Topics 1220 and 2588). The fact that the properties of a given real gas are not ideal is understood in terms of intermolecular interactions.

In understanding the properties of real liquid mixtures and real solutions, the classic approach identifies the properties of the corresponding systems where the thermodynamic properties are defined as 'ideal'. In the next stage the reasons why the properties of real liquid mixtures and real solutions are not ideal are discussed in terms of the nature and strength of intermolecular interactions. This general approach mimics the approach used to explain why the properties of real gases are not those of a defined ideal gas (see Topic 2588). In this context the van der Waals equation describing the differences between the properties of a real gas and an ideal gas sets the stage for theories describing the differences between the properties of real and ideal liquid mixtures and the properties of real and ideal solutions. Nevertheless we develop here the argument by considering the properties of a single gas, chemical substance j.

The starting points are two statements concerning an ideal gas.

I. The actual volume of the molecules making up an ideal gas is negligible compared to the total volume of the system.
II. Neither attractive nor long-range repulsive intermolecular forces are present.

In a real gas the molecular volume is not negligible. Also cohesive intermolecular forces mean that the pressure exerted on the containing vessel is less than in the case of an ideal gas. Therefore the equation of state requires that the pressure p is incremented by a quantity proportional to the density or, by a quantity inversely proportional to the volume. The famous van der Waals [1] equation takes the following form [2] where V_j is the molar volume of gas j at pressure p and temperature T.

$$\left(\mathrm{p}+\frac{\mathrm{a}}{\mathrm{V_j^2}}\right)\left(\mathrm{V_j}-\mathrm{b}\right)=\mathrm{R\,T}$$

The van der Waals equation has played an important role in the development of theories describing fluids; i.e. both liquids and gases. The equation has merit in that it involves just two constants, both characteristic of given chemical substance. Further as McGlashan notes, the equation never leads to physical nonsense and does not predict physically absurd results [3]. Similarly Rowlinson comments that the equation is easy to manipulate and never predicts physically absurd results [4]. Chue comments that despite its simplicity the van der Waals equation 'comprehends' both liquid and gaseous states [5].

However other authors are not so enthusiastic. For example, Prigogine and Defay comment that the equation is 'mainly of qualitative interest' [6]. Similarly Denbigh states that the a-parameter 'does not have a sound theoretical basis and interpretation of the a-parameter in terms of intermolecular attraction is 'intuitive' [7].

Perhaps the expectation that the $\mathrm{p-V-T}$ properties of all gases and liquids can be accounted for using two parameters characteristic of each chemical substance is too optimistic. Nevertheless there is merit in reviewing the van der Waals equation.

Equation (a) can be written as an equation for pressure p.

$$\mathrm{p}=\frac{\mathrm{R\,T}}{\mathrm{V_j}-\mathrm{b}}-\frac{\mathrm{a}}{\mathrm{V_j^2}}$$

This form of equation (a) highlights the role of the parameter b in describing the effect of molecular size and the role of parameter a in describing inter-molecular cohesion.

A plot of p as function of V_j at fixed temperature has an extremum at the point defined by equation (c) [8].

$$\frac{\mathrm{R\,T}}{\left(\mathrm{V_j}-\mathrm{b}\right)^2}=\frac{2\,\mathrm{a}}{\mathrm{V_j^3}}$$

Or,

$$\mathrm{T}=\frac{2\,\mathrm{a}\,\left(\mathrm{V_j}-\mathrm{b}\right)^2}{\mathrm{R\,V_j^3}}$$

Hence using equations (a) and (d) we obtain [9] an equation relating pressure p to V_j in terms of the two parameters

$$\mathrm{p} = \mathrm{a}\left[\frac{\mathrm{V_j} - 2\,\mathrm{b}}{\mathrm{V_j^3}}\right]$$

In a family of curves showing p as a function of V_j, one curve has a point of inflexion with a horizontal tangent where both $\frac{\partial p}{\partial V_m}$ and $\frac{\partial^2 p}{\partial V_m^2}$ are zero. This point is the **critical point** [10]. Interesting features based on the van der Waals equation characterise this point [11].

At the critical point [12,13],

$$V_j^c = 3\,b$$

$$p^c = a/27\,b^2$$

and

$$\mathrm{T^c} = 8\,\mathrm{a}/27\,\mathrm{R\,b}$$

A classic plot [10] describes the properties of a fixed amount of carbon dioxide in terms of isotherms showing the dependence of pressure on volume. This plot reported by T. Andrews in 1870 showed that $\mathrm{CO_2(g)}$ cannot be liquefied solely by the application of pressure at temperatures above 304.2 K. The latter is the critical temperature $\mathrm{T^c}$ for $\mathrm{CO_2}$, the critical pressure p_c being the pressure required to liquefy $\mathrm{CO_2}$ at this temperature. The molar volume at pressure $\mathrm{p^c}$ and temperature $\mathrm{T^c}$ is the critical molar volume $\mathrm{V_j^c}$.

The critical volume is obtained using the Law of Rectilinear Diameters originally described by L. Caillete and E. Mathias. The law requires that the mean density $\rho_\mathrm{j}(\mathrm{T})$ of gas and liquid states of a given chemical substance j at common temperature T is a linear function of T Thus,

$$\rho_\mathrm{j}(\mathrm{T}) = \rho_\mathrm{j}\,(\mathrm{T^c/K}) + \alpha\,(\mathrm{T/K})$$

The parameters $\rho_\mathrm{j}\,(\mathrm{T^c/K})$ and α are characteristic of chemical substance j; $\rho_\mathrm{j}\,(\mathrm{T^c/K})$ is the critical density of chemical substance j, leading to the critical molar volume $\mathrm{V_j}\,(\mathrm{T^c})$ at critical temperature $\mathrm{T^c}$ and critical pressure $\mathrm{p^c}$. Above the critical temperature the plot of pressure p and against molar volume at a given temperature T is a smooth curve. Below $\mathrm{T^c}$ and at low pressures, chemical substance j is a gas. With increase in pressure a stage is reached where a given system comprises two phases, gas and liquid. With further increase in pressure the system comprises a liquid. There is no sharp transition between liquid and gaseous states in contrast to that observed on melting a solid. In other words, gas and liquid states for chemical substance j form a **continuity of states**.

The **Law of Corresponding States** is an interesting concept, following an observation by J. D. van der Waals in 1881.

The pressure, volume and temperature for a given gas j are expressed in terms of the critical pressure $\mathrm{p_j^c}$, volume $\mathrm{V_j^c}$, and temperature $\mathrm{T_j^c}$ using three proportionality constants, β_1, β_2 and β_3 respectively. Thus

$$\mathrm{p} = \beta_1\,\mathrm{p_j^c}$$

$$\mathrm{V_j} = \beta_2\,\mathrm{V_j^c}$$

$$\mathrm{T_j} = \beta_3\,\mathrm{T_j^c}$$

Hence from equation (a),

$$\left(\beta_1\,p_j^c + \frac{a}{\left(\beta_2\,V_j^c\right)^2}\right)\left(\beta_2\,V_j^c - b\right) = R\,\beta_3\,T_j^c$$

Using equations (f), (g) and (h) for $\mathrm{p_j^c}$, $\mathrm{V_j^c}$ and $\mathrm{T_j^c}$ the following equation $j$is obtained from equation (m) [14].

$$\left(\beta_1 + \frac{3}{\beta_2^2}\right)(3\,\beta_2 - 1) = 8\,\beta_3$$

Equation (n) is the van der Waals reduced Equation of State for gas j; β_1, β_2 and β_3 being the reduced pressure, volume and temperature respectively. Significantly there are no parameters in equation (n) which can be said to be characteristic of a given

chemical substance. In other words the equation has a universal character [15].

The van der Waals equations prompted the development of many equations of state.

The van der Waals equation can be modified in two simple ways. In one modification it is assumed that $V_j \gg b$. The assumption is that attractive intermolecular processes are dominant Hence,

$$\left[\mathrm{p} + \frac{\mathrm{a}}{\mathrm{V_j^2}}\right] \mathrm{V_j} = \mathrm{R\,T}$$

Or,

$$\mathrm{p\,V_j} = \mathrm{R\,T} - (\mathrm{a}/\mathrm{V_j})$$

In another approach it is assumed that repulsive intermolecular forces are dominant. Thus,

$$\mathrm{p\,V_j} = \mathrm{R\,T} + \mathrm{p\,b}$$

Clausius Equation

One criticism of the van der Waal equation is that no account is taken of the possibility that parameters a and b can depend on temperature. Clausius suggested the following equation in which intermolecular attraction is described as inversely proportional to temperature; a, b and c are three constants characteristic of a gas j.

$$\left(\mathrm{p} + \frac{\mathrm{a}}{\mathrm{T}\,(\mathrm{V_j} + \mathrm{c})^2}\right)(\mathrm{V_j} - \mathrm{b}) = \mathrm{R\,T}$$

Nevertheless the advantages gained by recognising that attraction might be dependent on temperature are outweighed by problems associated with using this equation.

Bertholot Equation

In this approach, the term $(\mathrm{V}_j + c)$ in the Clausius equation is replaced by V_j. Then

$$\left(\mathrm{p} + \frac{\mathrm{a}}{\mathrm{T\,V_j^2}}\right)(\mathrm{V_j} - \mathrm{b}) = \mathrm{R\,T}$$

Or,

$$\mathrm{p\,V_j} = \mathrm{R\,T} + \mathrm{p\,b} - \frac{\mathrm{a}}{\mathrm{T\,V_j}} + \frac{\mathrm{a\,b}}{\mathrm{T\,V_j^2}}$$

The van der Waals, Clausius and Berthelot equations are the forerunners of a large family of cubic equations of state; i.e. equations of state that are cubic polynomials in molar volume.

Analysis of experimental data prompted the development of the following equation using critical pressure $\mathrm{p_j^c}$ and temperature $\mathrm{T_c}$.

$$\mathrm{p\,V_j} = \mathrm{R\,T}\left[1 + \frac{\mathrm{a}}{128}\frac{\mathrm{p\,T_j^c}}{\mathrm{p_j^c\,T}}\left(1 - 6\frac{\left(\mathrm{T_j^c}\right)^2}{\mathrm{T}^2}\right)\right]$$

Dieterici Equation

This modification suggested in 1899 by C. Dieterici attempts to account for the fact that molecules at the wall of a containing vessel have higher potential energy than molecules in the bulk gas. The following equation was proposed.

$$\mathrm{p}\,(\mathrm{V_j} - \mathrm{b}) = \mathrm{R\,T}\exp\left(-\frac{\mathrm{a}}{\mathrm{R\,T\,V_j}}\right)$$

The Virial Equation of State

The following virial equation was proposed in 1885 by Thiesen.

$$\mathrm{p\,V_j = R\,T\left[1 + \frac{B(T)}{V_j} + \frac{C(T)}{V_j^2} + \ldots\ldots\right]}$$

Following a suggestion in 1901 by H. K. Onnes, B(T), C(T),… are called **virial coefficients**. A modern account of equations of state is given in reference [16].

Boyle Temperature

Boyle's Law requires that the product $\mathrm{p\,V_j}$ at fixed temperature is independent of pressure. In the case of hydrogen, the product $\mathrm{p\,V_j}$ at $273\ \mathrm{K}$ increases with increase in pressure. However for many gases (e.g. nitrogen and carbon dioxide) the product $\mathrm{p\,V_j}$ at fixed T decreases with increase in pressure, passes through a minimum and then increases. For a given gas the minimum moves to lower pressures with increase in temperature until at high temperatures no minimum is observed. This is the Boyle temperature, which is characteristic of a given gas [11a]. The van der Waals equation offers an explanation of the pattern. Thus from equation (b),

$$\mathrm{p\,V_j = R\,T\left(\frac{V_j}{V_j - b}\right) - \frac{a}{V_j}} \qquad (1.14.26.1)$$

Equation 1.14.26.1 is differentiated with respect to pressure at constant temperature. If the plot of $\mathrm{p\,V_j}$ against p passes through zero at temperature $\mathrm{T_B}$, then $\mathrm{T_B}$ is given by equation (y) [17].

$$\mathrm{T_B = a/R\,b}$$

Therefore in terms of Equation (a), a low Boyle temperature is favoured by small a and large b parameters.

Footnotes

[1] For a reproduction of a portrait of Johannes van der Waals (1837-1923) see D. Kondepudi and I. Prigogine, Modern Thermodynamics, Wiley , Colchester, 1998, page 15.

$V_j = [m^3\ \mathrm{mol}^{-1}] \quad b = [\mathrm{m}^3\ \mathrm{mol}^{-1}]$

[2] $\left(\mathrm{p} + \frac{\mathrm{a}}{\mathrm{V_j^2}}\right) = \left([\mathrm{Nm}^{-2}] + \frac{\mathrm{a}}{[\mathrm{m}^3\ \mathrm{mol}^{-1}]^2}\right)$

Then, $\mathrm{a} = [\mathrm{Nmm}^{-2}]\ [\mathrm{m}^3\ \mathrm{mol}^{-1}]^2 = [\mathrm{Nmol}^{-2}\ \mathrm{m}^4]$
$\mathrm{R}\,T = [\mathrm{JmolK}^{-1}]\ [\mathrm{K}] = [\mathrm{Jmol}^{-1}]$

Then $\left([\mathrm{Nm}^{-2}] + \frac{[\mathrm{Nmol}^{-2}\ \mathrm{m}^4]}{[\mathrm{mol}^{-1}\ \mathrm{m}^3]^2}\right)\ [[\mathrm{m}^3\ \mathrm{mol}^{-1}] - [\mathrm{m}^3\ \mathrm{mol}^{-1}]]$
$= ([\mathrm{Nm}^{-2}] + [\mathrm{Nm}^{-2}])\ [\mathrm{m}^3\ \mathrm{mol}^{-1}] = [\mathrm{Nmmol}^{-1}] = [\mathrm{Jmol}^{-1}]$

[3] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979, page 176.

[4] J. S. Rowlinson, Liquids and Liquid Mixtures, Butterworths, London, 2nd edn., 1969, page 66.

[5] S. H. Chue, Thermodynamics, Wiley, Chichester, 1977, page 136.

[6] I. Prigogine and R. Defay, Chemical Thermodynamics, transl. D.H.Everett, Longmans Green, London, 1954, p. 145.

[7] K. Denbigh, The Principles of Chemical Equilibrium, Cambridge University Press. 3rd. edn. 1971, page 119.

[8] $\frac{\mathrm{dp}}{\mathrm{dV}} = -\frac{\mathrm{R\,T}}{(\mathrm{V_j - b})^2} + \frac{2\,\mathrm{a}}{\mathrm{V_j^3}}$ At an extremum, $\frac{\mathrm{dp}}{\mathrm{dV_j}} = 0$; then, $\frac{\mathrm{R\,T}}{(\mathrm{V_j - b})^2} = \frac{2\,\mathrm{a}}{\mathrm{V_j^3}}$

[9] $\left(p + \frac{a}{V_j^2}\right)(V_j - b) = R\,2\,a\,\frac{(V_j - b)^2}{V_j^3}$

$p + \frac{a}{V_j^2} = 2\,a\,\frac{(V_j - b)}{V_j^3}$

Or, $\mathrm{p} = \mathrm{a}\left[\frac{2\,\mathrm{V_j} - 2\,\mathrm{b} - \mathrm{V_j}}{\mathrm{V_j^3}}\right]$

[10] T.Andrews, Phil. Mag.,1870,[4],**39**,150.

[11] See for example,

a. S. Glasstone, Textbook of Physical Chemistry, MacMillan, London, 1948, 2nd. edn., page 435.
b. N. K.Adam, Physical Chemistry, Oxford, 1956, page 83; CO_2.
c. J. K. Roberts and A. R. Miller, Heat and Thermodynamics, Blackie, London, 1951, page 110; CO_2.
d. P. A . Rock, Chemical Thermodynamics, MacMillan, Toronto, 1969; H_2O.
e. E. F. Caldin, Chemical Thermodynamics, Oxford, 1958, chapter III.
f. J. S. Winn, Physical Chemistry, Harper Collins, New York, 1995, chapter 1.
g. M. L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979, page 132; xenon.
h. P. Atkins and J. de Paula, Physical Chemistry, Oxford, 2002, 7th edn., Section 1.4.

[12] We rewrite equation (e) in the following form. $p = a\ [V_j - 2\,b]\ V_j^{-3}$

Or, $\mathrm{p = a\ \left\{[V_j - 2\,b]\ \left[V_j^{-3}\right]\right\}}$

Then
$$\begin{aligned}\frac{\mathrm{dp}}{\mathrm{dV}} &= \mathrm{a\ \left[V_j^{-3} + (V_j - 2\,b)\ (-3)\,V_j^{-4}\right]}\\ &= \mathrm{a\ \left[V_j^{-3} - 3\,V_j^{-3} + 6\,b\,V_j^{-4}\right]}\\ &= \mathrm{a\ \left[-2\,V_j^{-3} + 6\,b\,V_j^{-4}\right]}\end{aligned}$$

$\frac{dp}{dV_j} = 0$ where $\left[-2\,V_j^{-3} + 6\,b\,V_j^{-4}\right] = 0$ Or, $\frac{1}{V_j^3} = \frac{3\,b}{V_j^4}$ Or, $V_j^c = 3\,b$ From equation (e), $p^c = \frac{a\,b}{27\,b^3}$ or, $\mathrm{p^c = \frac{a}{27\,b^2}}$

Then from equation (d), $T^c = \frac{2\,a\,(3\,b-b)^2}{R\,27\,b^3} = \frac{8\,a\,b^2}{27\,R\,b^3} = \frac{8\,a}{27\,R\,b}$

[13]

$$\begin{aligned}\mathrm{V_j^c = 3\,b = [1]\ \left[m^3\ mol^{-1}\right] = \left[m^3\ mol^{-1}\right]}\\ \mathrm{p^c = \frac{\left[Nm^4\ mol^{-2}\right]}{[1]\ \left[m^3\ mol^{-1}\right]^2} = \left[Nm^4\ m^{-6}\ mol^{-2}\ mol^2\right] = \left[Nm^{-2}\right]}\\ \mathrm{T^c = \frac{[1]\ \left[Nmmol^{-2}\right]}{[1]\ [Jmolm^{-1}]\ \left[m^3\ mol^{-1}\right]} = \frac{[Nm]}{[Nm]}\,[K] = [K]}\end{aligned}$$

[14] $\left[\beta_1\,\frac{\mathrm{a}}{27\,\mathrm{b}^2} + \frac{\mathrm{a}}{(\beta_2\,3\,\mathrm{b})^2}\right]\ [\beta_2\,3\ \mathrm{b} - \mathrm{b}] = \mathrm{R}\,\frac{8\,\mathrm{a}\,\beta_3}{27\,\mathrm{R\,b}}$

[15] F. T. Wall, Chemical Thermodynamics, W. H. Freeman, San Francisco, 1965, page 169.

[16] S. I. Sandler, H. Orbey and B.-I. Lee , Models for Thermodynamics and Phase Equilibria Calculations , ed. S. I. Sandler, Marcel Dekker, New York, 1994, pp.87-186.

[17]

$$\begin{aligned}\mathrm{p\,V_j} &= \mathrm{R\,T\,\frac{V_j}{V_j - b} - \frac{a}{V_j}}\\ \left[\frac{\partial\,(\mathrm{p\,V_j})}{\partial \mathrm{p}}\right] &= \left[\mathrm{R\,T}\left(\frac{1}{\mathrm{V_j - b}}\right) - \mathrm{R\,T}\left(\frac{\mathrm{V_j}}{(\mathrm{V_j - b})^2}\right) + \frac{\mathrm{a}}{\mathrm{V_j^2}}\right]\left(\frac{\partial \mathrm{V_j}}{\partial \mathrm{p}}\right)_{\mathrm{T}}\end{aligned}$$

Then at $\left[\frac{\partial(\mathrm{p\,V_j})}{\partial \mathrm{p}}\right] = 0$,

$$\left[RT\left(\frac{V_j - b - V_j}{(V_j - b)^2}\right) + \frac{a}{V_j^2}\right] = 0$$

Or, $RT = \frac{a}{b}\,\frac{(V_j - b)^2}{V_j^2}$

If the minimum occurs where p is zero (i.e. where V_j is infinitely large), $\mathrm{R\,T_B = a/b}$

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1.14.27: Euler's Theorem

This theorem emerges from theories concerned with differential equations. The theorem finds many applications in thermodynamics. In particular the theorem concerned with homogeneous functions of the first degree is important. This theorem can be stated as follows [1].

$$\mathrm{f(k\,x, k\,y, k\,z) = k\,f(x, y, z)} \tag{1.14.27.1}$$

By way of illustration we consider a liquid mixture volume V prepared using $\mathrm{n_1}$ and $\mathrm{n_2}$ moles of liquid 1 and 2. If we had used $2.\mathrm{n_1}$ and $2.\mathrm{n_2}$ moles of liquids 1 and 2, then the final volume would have been $2.\mathrm{V}$. The important theorem allows us to set down the following descriptions.

For a system comprising i-chemical substances, it follows that

$$\mathrm{V} = \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{n_j\,V_j} \tag{1.14.27.2}$$

where partial molar volume

$$\mathrm{V_j} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}} \tag{1.14.27.3}$$

It should be noted that some thermodynamic monographs, when citing Equation 1.14.27.2, include the phrase ‘at constant temperature and pressure’. Other monographs do not include this phrase on the grounds that the isobaric - isothermal condition is included in the definition of the partial derivative in Equation 1.14.27.3. In practice nothing is lost by including this phrase simply to indicate that the analysis is concerned with the properties of systems in the $\mathrm{T–p}$ - composition domain.

A similar analysis in the context of Gibbs energies leads to the following two equations and the definition of chemical potentials.

$$G = \sum_{j=1}^{j=i} n_j\,\mu_j \tag{1.14.27.4}$$

where chemical potential

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{T,p,n(i\neq j)} \tag{1.14.27.5}$$

Footnotes

[1] R. J. Tykodi, J. Chem. Educ.,1982,**59**,557.

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1.14.28: First Law of Thermodynamics

The first law of thermodynamics centres on the concept of energy. In its broadest sense, the law requires that the energy of the universe is constant. This is a rather overwhelming statement. A more attractive statement requires that the (internal) thermodynamic energy U of a chemistry laboratory is constant:

$$\mathrm{U} = \text{ constant}$$

The latter statement is the **principle of conservation of energy**; energy can be neither created nor destroyed. All that a chemist can do, during an experiment using a closed reaction vessel, is to watch energy 'move ' between system and surroundings. As a consequence of equation (a), we state that

$$\Delta \mathrm{U}(\text{ system }) = -\Delta \mathrm{U}(\text{ surroundings })$$

We can not know the actual energy of a closed system although we know that it is an extensive property of the system [1]. In describing energy changes we need a convention. So we use the acquisitive convention describing all changes in terms of how a system is affected. Thus the statement $\Delta \mathrm{U} < 0$ means that the energy of a given system decreases during a given process; e.g. chemical reaction.

Footnote

[1] In principle it is possible to know the total energy of a given system using a scale in conjunction with Einstein's famous equation, $\mathrm{E} = \mathrm{m}\,\mathrm{c}^2$. However, the mass corresponding to 1 kJ is only about 10^{-14} kg.

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1.14.29: Functions of State

One Chemical Substance

For a **system** containing one chemical substance we define the volume using equation (a).

$$\mathrm{V} = \mathrm{V}[\mathrm{T}, \mathrm{p}, \mathrm{n},] \tag{a}$$

The variables in the square brackets are the **Independent Variables**. The term `independent' means that, within limits [1], we can change T independently of the pressure and n_j; change p independently of T and n_j; and n_i independently of T and p. There are some restrictions in our choice of independent variables. At least one variable must define the amount of all substances in the system and one variable must define the `hotness' of the system.

Actually there is merit in writing equation (a) in terms of three intensive variables which in turn define, for example the, the molar volume of liquid chemical substance 1 at specified temperature and pressure, $\mathrm{V}_1^*(\ell)$.

$$\mathrm{V}_1^*(\ell) = \mathrm{V}(\ell)\,[\mathrm{T}, \mathrm{p}, \mathrm{x}_1 = 1]$$

Two Chemical Substances

If the chemical composition of a given closed system is specified in terms of two chemical substances 1 and 2, four independent variables $[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2]$ define the dependent variable V [2]. Thus

$$\mathrm{V} = \mathrm{V}\,[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2]$$

i - Chemical Substances

For a system containing i-chemical substances where the amounts can be independently varied, the dependent variable V is defined by the following equation.

$$\mathrm{V} = \mathrm{V}\,[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2 \ldots \mathrm{n}_\mathrm{i}]$$

In a general analysis, we start out with a closed system having Gibbs energy at temperature T and pressure p, molecular composition (organisation) ξ and affinity for spontaneous change A. We define the Gibbs energy as follows.

$$\mathrm{G} = \mathrm{G}[\mathrm{T}, \mathrm{p}, \boldsymbol{\xi}]$$

In the state defined by equation (e), there is an affinity for spontaneous change (chemical reaction) A. We imagine that starting with the system in the state defined by equation (e), it is possible to change the pressure and perturb the system to a series of neighbouring states for which the affinity for spontaneous change remains constant. The differential dependence of G on pressure for the original state along the path at constant affinity is given by $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T,A}}$.

Returning to the original state characterised by T, p and ξ, we imagine it is possible to perturb the system by a change in pressure in such a way that the system remains at fixed extent of reaction ξ. The differential dependence of G on pressure for the original state along the path at constant ξ is given by $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T},\xi}$. We explore these dependences of G on pressure at fixed temperature and at (i) fixed composition ξ and (ii) fixed affinity for spontaneous change, A. $(\partial G/\partial p)_{\mathrm{T,A}}$ and $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T},\xi}$ are related using a standard calculus operation [1]. Thus at fixed temperature,

$$\left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\mathrm{A}} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\xi} - \left[\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right]_{\xi}\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{p}}\left[\frac{\partial \mathrm{G}}{\partial \xi}\right]_{\mathrm{p}}$$

This interesting equation shows that the differential dependence of Gibbs energy (at constant temperature) on pressure at constant affinity for change does **NOT** equal the corresponding dependence at constant extent of chemical reaction. This is inequality is not surprising. But our interest is drawn to the case where the system under discussion is, at fixed temperature and pressure, at thermodynamic equilibrium where A is zero, $\mathrm{d}\xi/\mathrm{dt}$ is zero, the Gibbs energy is a minimum **AND** significantly $(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}}$ is zero. We conclude that

$$\mathrm{V} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\mathrm{T,A}=0} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\mathrm{T},\xi(\mathrm{eq})}$$

This rather long winded argument confirms that volume V is a state variable, the dependence of G on pressure for differential displacement at constant '$\mathrm{A}=0$' and $\sim^{e} q$ being identical. These comments may seem trivial but the point is made if we go on to consider the volume of a system as a function of temperature at constant pressure. We again use a calculus operation [1] to derive the relationship in equation (h).

$$\left[\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right]_{\mathrm{A}}=\left[\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right]_{\xi}-\left[\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right]_{\xi}\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{p}}\left[\frac{\partial \mathrm{V}}{\partial \xi}\right]_{\mathrm{p}}$$

We are not surprised to discover that in general terms the differential dependence of V on temperature at constant affinity does not equal the differential dependence of V on temperature at constant composition/organisation. Indeed unlike the simplification we used in connection with equation (e), we cannot assume that the volume of reaction $(\partial \mathrm{V}/\partial \xi)_{\mathrm{T},pp}$ is zero at equilibrium. In other words for a closed system at thermodynamic equilibrium at fixed T and fixed p {where $\mathrm{A}=0, \xi=\xi^{\mathrm{eq}}$ and $\mathrm{d}\xi/\mathrm{dt}=0$}, there are two thermal expansions [2].

We consider a closed system in equilibrium state I defined by the set of variables, $\{\mathrm{T[I]}, \mathrm{p}, \mathrm{A}=0, \xi^{\mathrm{eq}}[\mathrm{I}]\}$. The equilibrium composition is represented by $\xi^{\mathrm{eq}}[\mathrm{I}]$ at zero affinity for spontaneous change. This system is perturbed to nearby state at constant pressure .

a. The state I is displaced to a nearby equilibrium state II defined by the set of variables $\{\mathrm{T[I]}+\delta \mathrm{T}, \mathrm{p}, \mathrm{A}=0, \xi^{\mathrm{eq}}[\mathrm{I}]\}$. This equilibrium displacement is characterised by a volume change.

$$\Delta \mathrm{V}(\mathrm{A}=0)=\mathrm{V[II]}-\mathrm{V[I]}$$

$$\mathrm{E}(\mathrm{A}=0)=\left[\frac{\mathrm{V(II)}-\mathrm{V(I)}}{\Delta \mathrm{T}}\right]$$

The equilibrium expansivity,

$$\alpha(\mathrm{A}=0)=\mathrm{E})\mathrm{A}=0)/\mathrm{V}$$

In order for the system to move from one equilibrium state, I with composition $\xi^{\mathrm{eq}}[\mathrm{I}]$ to another equilibrium state, II with composition $\xi^{\mathrm{eq}}[\mathrm{II}]$, the chemical composition and /or molecular organisation changes. The term `expansion' indicates the isobaric dependence of volume on temperature,

$$\mathrm{E}=\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}=\left[\mathrm{m}^{3}\ \mathrm{K}^{-1}\right]$$

E is an extensive variable. The corresponding volume intensive variable is the expansivity, α.

$$\alpha=\frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{p}$$

where $\alpha=\frac{1}{[\mathrm{m}^{3}]}\left[\frac{\mathrm{m}^{3}}{\mathrm{K}}\right]=[\mathrm{K}^{-1}]$

b.

Hence we define the `frozen' expansion, $\mathrm{E}(\sim=\ \text{fixed}\ )$. An alternative name is the instantaneous expansion because, practically, we would have to change the temperature at such a high rate that there is no change in molecular composition or molecular organisation in the system. Thus,

$$\mathrm{E}(\xi=\ \text{fixed}\ )=\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi}$$

Further

$$\alpha(\xi=\ \text{fixed}\ )=\frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi}$$

Similar comments apply to isothermal compressibilities, κ_{T}; there are two limiting properties, $\kappa_{\mathrm{T}}(\mathrm{A}=0)$ and $\kappa_{\mathrm{T}}(\xi)$. In order to measure $\kappa_{\mathrm{T}}(\xi)$ we have to change the pressure in a infinitely short time.

The entropy S at fixed composition is given by the partial differential $-\left(\frac{\partial G}{\partial T}\right)_{p,5}$ and, at constant affinity of spontaneous change by $-\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{p,A}}$. At equilibrium where $\mathrm{A}=0$, the equilibrium entropy, $S(A=0)=-\left(\frac{\partial G}{\partial T}\right)_{p,A=0}$. We carry over the argument described above but now concerned with a system characterised by $\mathrm{T,p},\xi$ which is perturbed by a change in temperature. We consider two pathways, at constant A and at constant ξ.

$$\left[\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right]_{\mathrm{p,A}}=\left[\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}-\left[\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{T,p}}\left[\frac{\partial \mathrm{G}}{\partial \xi}\right]_{\mathrm{T,p}}$$

But at equilibrium, A which equals $-\left[\frac{\partial G}{\partial \xi}\right]_{\mathrm{T,p}}$ is zero and so $\mathrm{S}(\mathrm{A}=0)=\mathrm{S}\left(\xi^{\mathrm{eq}}\right)$. Then just as for volumes, the entropy of a system is not a property concerned with pathways between states; entropy is a function of state.

Another important link involving Gibbs energy and temperature is provided by the Gibbs-Helmholtz equation. We explore the relationship between changes in $(\mathrm{G/T})$ at constant affinity and fixed ξ following a change in temperature. Thus,

$$\left[\frac{\partial(\mathrm{G/T})}{\partial \mathrm{T}}\right]_{\mathrm{p,A}}=\left[\frac{\partial(\mathrm{G/T})}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}-\frac{1}{\mathrm{T}}\left[\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{T,p}}\left[\frac{\partial \mathrm{G}}{\partial \xi}\right]_{\mathrm{T,p}}$$

But at equilibrium A which equals $-(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}}$ is zero. Then $\mathrm{H}(\mathrm{A}=0)=\mathrm{H}\left(\xi^{\mathrm{eq}}\right)$.

In other words the variable, enthalpy is a function of state. This is not the case for isobaric heat capacities. Thus,

$$\left[\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right]_{\mathrm{p,A}}=\left[\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}-\left[\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right]_{\mathrm{p},\xi}\left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{T,p}}\left[\frac{\partial \mathrm{H}}{\partial \xi}\right]_{\mathrm{T,p}}$$

We cannot assume that the triple product term in equation (q) is zero. Hence there are two limiting isobaric heat capacities; the equilibrium isobaric heat capacity $\mathrm{C_p}(\mathrm{A}=0)$ and the `frozen' isobaric heat capacity $\mathrm{C_p}\left(\xi^{\mathrm{eq}}\right)$. In other words, an isobaric heat capacity is not a function of state because it is concerned with a pathway between states.

Footnotes

[1] The phrase `independent variable' is important. With reference to the properties of an aqueous solution containing ethanoic acid, the number of components for such a solution is 2, water and ethanoic acid. The actual amounts of ethanoic acid, water, ethanoate and hydrogen ions are determined by an equilibrium constant which is an intrinsic property of this sytem at a given T and p. From the point of view of the Phase Rule, the number of components equals two. For the same reason when we consider the volume of a system containing n moles of water we do not take account of evidence that water partly self-dissociates into $\mathrm{H^+(aq)}$ and $\mathrm{OH^-(aq)}$ ions.

[2] In terms of the Phase Rule, we note that for two components (C = 2) and one phase (P = 1) , the number of degrees of freedom F equals equals two. These degrees of freedom refer to intensive variables. Hence for a solution where chemical substance 1 is the solvent and chemical substance 2 is the solute, the system is defined by specifying by the three (intensive) degrees of freedom, \ (\mathrm{T}, \mathrm{p} and, for example, solute molality.

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1.14.30: Heat, Work, and Energy

Thermodynamics asserts that the energy of a closed system increases if

i. heat q flows from the surroundings into a system and
ii.

Separation of the heat term from the work term is extremely important in the context of the Second Law of Thermodynamics. Heat flows spontaneously from high to low temperatures, the word 'spontaneous' being absolutely crucial in the context of the Second Law.

There are many ways in which the surroundings can do work on a system. At this stage we note the distinction which is drawn between the three variables U, q and w. [The point is emphasized by use of upper and lower case letters.] The variables q and w describe pathways which can result in a change in thermodynamic energy. We make the point by rewriting equation (a) to show the change in thermodynamic energy on going from state I to state II. Thus,

$$\Delta \mathrm{U} = \mathrm{U(II)} - \mathrm{U(I)} = \mathrm{q} + \mathrm{w}$$

If for example $\Delta \mathrm{U} = 100\ \mathrm{J}$, this can be a consequence of many pathways between state I and state II: e.g.

a. $\mathrm{q} = 50\ \mathrm{J},\ \mathrm{w} = 50\ \mathrm{J}$,
b. $\mathrm{q} = 0\ \mathrm{J},\ \mathrm{w} = 100\ \mathrm{J}$ and
c. $\mathrm{q} = 150\ \mathrm{J},\ \mathrm{w} = -50\ \mathrm{J}$.

Hence U is a function of state (or, state variable) although q and w are not state variables. This is a triumph of the First Law of Thermodynamics. The task faced by chemists is to identify and describe quantitatively the actual pathway accompanying, for example, a given chemical reaction. Equation (a) signals the energy difference $\Delta \mathrm{U}$ between two states which might involve a comparison of the energies at the start and finish of a chemical reaction in a closed system. In developing our argument there is merit in considering the change in energy of the original system following a small change along the overall reaction pathway.

We consider a closed reaction vessel containing ethyl ethanoate (aq; $0.1\ \mathrm{mol}$) and NaOH(aq; excess) . Spontaneous chemical reaction leads to hydrolysis of the ester to form EtOH(aq). The change in thermodynamic energy $\Delta \mathrm{U}$ equals $\mathrm{U(II)} - \mathrm{U(I)}$. We subdivide the total chemical reaction into small steps where the change in composition, (i.e. $\mathrm{d}\xi$) is accompanied by a change in thermodynamic energy dU.

$$\Delta \mathrm{U} = \int_{\text{state I}}^{\text{state II}} \mathrm{dU}$$

If the volume of the system changes by the differential amount dV such that the pressure within the closed system equals the confining pressure p [2],

$$\mathrm{w} = -\mathrm{p}\,\mathrm{dV}$$

Then [3],

$$\mathrm{dU} = \mathrm{q} - \mathrm{p}\,\mathrm{dV}$$

We write equation (e) in the following form;

$$\mathrm{q} = \mathrm{dU} + \mathrm{p}\,\mathrm{dV}$$

The right hand side of equation (f) contains the differential changes in two extensive state variables, U and V. Consequently heat q is precisely defined by the changes in thermodynamic energy and volume at pressure p.

Footnotes

[1] The 'equivalence ' of heat and work was first demonstrated in many experiments carried out in the 19th Century by James Joule, the son of a brewer (Salford, England). Joule showed that by doing work on a thermally isolated system the temperature of the latter increases. In other words, doing work on a system is equivalent to passing heat into the system.

The SI unit of energy is the joule, symbol J; $\mathrm{J} \equiv \mathrm{kgm}^2\ \mathrm{s}^{-2}$ Sometimes one reads that thermodynamics is not concerned with ‘time’. However the concept of energy and the unit of energy involves ’time’. Of course the origins of these concepts are classical mechanics and accompanying discussion of potential and kinetic energies.

[2] $\mathrm{p\,V} = [\mathrm{Nm}^{-2}]\ [\mathrm{m}^3] = [\mathrm{Nm}] = [\mathrm{J}]$

[3] The fundamental link between heat and work was established by Joule. Interestingly the link between heat and work was apparent previously to A. Haller who suggested that human bodies are heated by the friction between solid particles in the blood passing through the capillaries in the lungs; see comments by

a. P. Epstein, Textbook of Thermodynamics, Wiley, New York, 1937.
b. M. A. Paul, Principles of Chemical Thermodynamics, McGraw-Hill, New York, 1957, p52.

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1.14.31: Helmholtz Energy

Gibbs energy is defined with practical chemistry in mind because the definition centres on closed systems held at constant temperature and constant pressure. A similar interest prompt definition of the Helmholtz energy, symbol F. By definition,

$$\mathrm{F} = \mathrm{U} - \mathrm{T}\,\mathrm{S}$$

Physicists use the term 'Helmholtz Function'. The old term 'Helmholtz free energy' is not encouraged [1]. If a closed system is displaced to a neighboring state, the differential change in Helmholtz energy is given by equation (b).

$$\mathrm{dF} = \mathrm{dU} - \mathrm{T}\,\mathrm{dS} - \mathrm{S}\,\mathrm{dT}$$

But the differential change in thermodynamic energy is given by the Master Equation. By incorporating the latter into equation (b), we obtain equation (c), the memorable "all-minus" equation.

$$\mathrm{dF} = -\mathrm{S}\,\mathrm{dT} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi$$
$$\mathrm{A}\,\mathrm{d}\xi \geq 0$$

At fixed temperature and fixed volume (isothermal and isochoric conditions),

$$\mathrm{dF} = -\mathrm{A}\,\mathrm{d}\xi$$

All spontaneous processes at fixed temperature and fixed volume lower the Helmholtz energy of a closed system. In practical terms, for a closed system held at constant volume and temperature, chemical reaction (molecular reorganization) lowers the Helmholtz energy of the system [2]. We presume that the pressure inside the reaction vessel will change, decreasing for some systems and increasing for other systems. As it stands thermodynamics offers no generalization concerning how the pressure changes. In fact if we want to use the Helmholtz energy as an indicator of the direction of spontaneous change we would build the reaction vessel with thick steel walls. This is a practical possibility and so the Helmholtz energy is a practical thermodynamic potential. For equilibrium transformations (i.e. at constant A = zero),

$$S = -\left(\frac{\partial \mathrm{F}}{\partial \mathrm{T}}\right)_{\mathrm{V,A=0}}$$

Similarly [3]

$$\mathrm{p} = -\left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}}\right)_{\mathrm{T,A=0}}$$

Footnotes

[1] Since the product $\mathrm{T}\,\mathrm{S}$ is the linked energy, equation (a) shows that F is the 'free energy' of the system.

[2] An interesting literature discusses the analysis of experimental data in terms of an isochoric condition.

a. Liquid transport; A. F. M. Barton, Rev. Pure Appl. Chem., 1971, **21**, 49.
b. Ionic Conductances in Solution. F. Barreira and G. J. Hills, Trans. Faraday Soc.,1968, **64**,1539, and references therein
c. Chemical kinetics
   i. M. G. Evans and M. Polanyi, Trans. Faraday Soc.,1935, **31**, 873.
   ii. E. Whalley, Ber. Bunsenges. Phys. Chem., 1966. **70**, 958, and references therein.
   iii. P. G. Wright, J. Chem. Soc. Faraday Trans. 1, 1986, **82**, 2557, and 2563.
   iv. L. M. P. C. Albuquerque and J. C. R. Reis, J. Chem. Soc. Faraday Trans.1, 1989, **85**, 207; 1991, **87**, 1553.
   v. J. B. F. N. Engberts, J. R. Haak, M. J. Blandamer, J. Burgess and H. J. Cowles, J. Chem. Soc .Perkin Trans, 2.1990,1059, and references therein.
d. Chemical Equilibria. M. J. Blandamer, J. Burgess, B. Clarke and J. M. W. Scott, J. Chem. Soc. Faraday 1984, **80**, 3359, and references therein..

[3] A similar set of equations describes the differential change in F at constant molecular composition (molecular organization). Thus

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,\xi} \text{ and, } p = -\left(\frac{\partial F}{\partial V}\right)_{T,\xi}$$

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1.14.32: Hildebrand Solubility Parameter

The cohesive energy density (c.e.d.) of a liquid is defined by equation (a).

$$\text{c.e.d.} \ = \Delta_{\text{vap}} \, \text{U}^0 / \text{V}^*(\ell)$$

$\Delta_{\text{vap}} \, \text{U}^0$ is the change in thermodynamic energy when one mole of a given chemical substance passes from the liquid to the vapor state. The square root of the c.e.d. for liquid j is the Hildebrand solubility parameter for that liquid.

$$\delta = (\ \text{c.e.d.}\ )^{1/2}$$

δ can be expressed in many units but following the original definition the customary unit is $\left(\text{cal}^{1/2} \ \text{cm}^{-3/2}\right)$. Property δ provides an estimate of cohesion within a given liquid. The idea goes a little further in terms of understanding solubilities. A clever idea is based on the following argument.

Consider two liquids A and B. We want to take a small sample of liquid A (as a solute) and dissolve in liquid B as the solvent. Within liquid A the intermolecular interactions A ... \(A are responsible for the cohesion within this chemical substance. Similarly within liquid B, B − B intermolecular forces are responsible for the cohesion within liquid B. If B − B interactions are much stronger than A − A and A − B intermolecular interactions it is likely that A will not be soluble in liquid B. Similarly if A − A interactions are stronger than B − B and A − B interactions it is likely that A will not be soluble in liquid B. If substance A is to be soluble in liquid B, their cohesive energy densities should be roughly equal.

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1.14.33: Infinite Dilution

The term 'infinite dilution' is often encountered in reviewing the properties of solutions. However some caution has to be exercised when this term is used [1]. There is merit in distinguishing between the properties of aqueous solutions containing simple neutral solutes and those containing salts because the impact of solute - solute interactions plays an important role in the analysis. Further we need to distinguish the properties of solutes and solvents.

Neutral Solutes: The Solute

The chemical potential of solute j, $\mu_j(\mathrm{aq})$ is related to the composition of the solution, molality m_j, at temperature T and pressure p which is assumed to be close to the standard pressure.

$$\mu_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_{\mathrm{j}}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right)$$

Or

$$\mu_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\right) + \mathrm{R}\,\mathrm{T}\,\ln\left(\gamma_{\mathrm{j}}\right)$$

For simple solutes in aqueous solutions, $\ln(\gamma_j)$ is a linear function of the molality m_j.

$$\ln\left(\gamma_{\mathrm{j}}\right) = \chi\,\left(\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\right)$$

Here χ is a function of temperature and pressure.

$$\mu_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) + \mathrm{R}\,\mathrm{T}\,\ln\left(\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\right) + \mathrm{R}\,\mathrm{T}\,\chi\,\left(\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\right)$$

We note therefore that

$$\mathrm{limit}\,(\mathrm{m}_j \to 0)\,\mu_j(\mathrm{aq};\mathrm{T};\mathrm{p}) = -\infty$$

Hence with increasing dilution of the solution, solute j is increasingly stabilised, $\mu_j(\mathrm{aq};\mathrm{T};\mathrm{p})$ decreasing to '$-\infty$' in an infinite amount of solvent Using the Gibbs-Helmholtz Equation, equation (a) yields equation (f).

$$-\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p})/\mathrm{T}^{2} = -\mathrm{H}_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p})/\mathrm{T}^{2} + \mathrm{R}\,\left(\partial\ln\left(\gamma_{\mathrm{j}}\right)/\partial\mathrm{T}\right)_{\mathrm{p}}$$

$\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p})$ is the partial molar enthalpy of solute j.

$$\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{H}_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) - \mathrm{R}\,\mathrm{T}^{2}\,\left(\partial\ln\left(\gamma_{\mathrm{j}}\right)/\partial\mathrm{T}\right)_{\mathrm{p}}$$

Using equation (c),

$$\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{H}_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) - \mathrm{R}\,\mathrm{T}^{2}\,\left(\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\right)\,\left(\partial\chi/\partial\mathrm{T}\right)_{\mathrm{p}}$$

Hence,

$$\mathrm{limit}\,(\mathrm{m}_{\mathrm{j}} \to 0)\,\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{H}_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p})$$

As the solution becomes more dilute and **approaches** infinite dilution so $\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p})$ in the limit of infinite dilution approaches the partial molar enthalpy of solute j in the reference solution $\mathrm{H}_{\mathrm{j}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p})$.where the partial molar enthalpy is identified as $\mathrm{H}_{\mathrm{j}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p})$.$Granted the latter conclusion based on equation (h), this equation offers information concerning the form of the plot of \(\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p})$ against m_j.

$$\left[\partial\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p})/\partial\mathrm{m}_{\mathrm{j}}\right] = -\mathrm{R}\,\mathrm{T}^{2}\,\left(\mathrm{m}^{0}\right)^{-1}\,\left(\partial\chi/\partial\mathrm{T}\right)_{\mathrm{p}}$$

In other words the gradient of the plot of $\mathrm{H}_{\mathrm{j}}(\mathrm{aq};\mathrm{T};\mathrm{p})$ against m_j is finite, the gradient being determined by the sign of $(\partial\chi/\partial T)_p$.

The partial molar isobaric heat capacity of the solute j is given by the differential of equation (h) with respect to temperature.

$$\mathrm{C}_{\mathrm{pj}}(\mathrm{aq};\mathrm{T};\mathrm{p}) = \mathrm{C}_{\mathrm{pj}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p}) - \mathrm{R}\,\left(\mathrm{m}_{\mathrm{j}}/\mathrm{m}^{0}\right)\,\left[\frac{\partial}{\partial\mathrm{T}}\left(\mathrm{T}^{2}\,\left(\partial\chi/\partial\mathrm{T}\right)_{\mathrm{p}}\right)\right]$$

$\mathrm{Limit}\,(\mathrm{m}_{\mathrm{j}} \to 0)\,\mathrm{C}_{\mathrm{pj}}(\mathrm{aq};\mathrm{T};\mathrm{p})$ is a finite quantity, $\mathrm{C}_{\mathrm{pj}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p})$. In other words the limiting partial molar isobaric heat capacity of the solute $\mathrm{C}_{\mathrm{pj}}^{\infty}(\mathrm{aq};\mathrm{T};\mathrm{p})$ equals the standard partial molar isobaric heat capacity, $\mathrm{C}_{\mathrm{pj}}^{0}(\mathrm{aq};\mathrm{T};\mathrm{p})$.

$$\text{limit}\,(m_j \rightarrow 0)\, C_{pj}(aq;T;p) = C_{pj}^{\infty}(aq;T;p) = C_{pj}^{0}(aq;T;p)$$

A similar conclusion is reached when we turn our attention to partial molar volumes recognizing that for solute j,

$$V_j(aq;T;p) = V_j^0(aq;T;p) + R\,T\,\left(m_j/m^0\right)\,(\partial\chi/\partial p)_T$$

Therefore,

$$\text{limit}\,(m_j \rightarrow 0)\, V_j(aq;T;p) = V_j^0(aq;T;p)$$

The limiting value of $V_j(aq;T;p)$ is a finite quantity such that the limiting (i.e. infinite dilution) value of $V_j(aq;T;p)$, namely $V_j^{\infty}(aq;T;p)$ equals the standard partial molar volume, $V_j^0(aq;T;p)$.

The interesting question arises as to why the limiting values of partial molar enthalpies, volumes and isobaric heat capacities are real (and important) properties but limiting chemical potentials are not. We start again with equation (b) recalling that partial molar entropy $S_j = -\left(\partial\mu_j/\partial T\right)_p$.

$$S_j(aq;T;p) = \\ S_j^0(aq;T;p) - R\,\ln\left(m_j/m^0\right) - R\,\ln\left(\gamma_j\right) - R\,T\,\left(\partial\ln\left(\gamma_j\right)/\partial T\right)_p$$

But

$$\text{limit}\,(m_j \rightarrow 0)\,\ln\left(m_j/m^0\right) = \text{ minus infinity}$$

Then

$$\text{limit}\,(m_j \rightarrow 0)\, S_j = \text{ plus infinity}$$

With increase in dilution $S_j(aq;T;p)$ tends to the asymptotic limit, plus infinity. For a solution at fixed T and p prepared using 1 kg of water, the Gibbs energy is given by equation (r).

$$G\left(T;p;aq;w_1 = 1\text{ kg}\right) = \left(1/M_1\right)\,\mu_1(aq) + m_j\,\mu_j(aq)$$

Or,

$$G\left(T;p;aq;w_1 = 1\text{ kg}\right) = \left(1/M_1\right)\,\left[\mu_1^*(\ell) - \phi\,R\,T\,M_1\,m_j\right] \\ + m_j\,\left[\mu_j^0(aq) + R\,T\,\ln\left(m_j/m^0\right) + R\,T\,\ln\left(\gamma_j\right)\right]$$

$$\text{limit}\,(m_j \rightarrow 0)\, G\left(T;p;aq;w_1 = 1\text{ kg}\right) = \mu_1^*(\ell)/M_1$$

Salt Solutions; The Salt

We consider a dilute 1:1 salt solution, confining the analysis to a consideration of the impact of the Debye - Huckel Limiting Law (DHLL). For a salt solution, molality m_j,

$$\mu_j(aq;T;p) = \mu_j^0(aq;T;p) + 2\,R\,T\,\ln\left(m_j/m^0\right) + 2\,R\,T\,\ln\left(\gamma_{\pm}\right)$$

Or, using the DHLL

$$\mu_j(aq;T;p) = \\ \mu_j^0(aq;T;p) + 2\,R\,T\,\ln\left(m_j/m^0\right) - 2\,R\,T\,S_{\gamma}\,\left(m_j/m^0\right)^{1/2}$$

From equation (u),

$$\left[\frac{\partial\mu_j(aq;T;p)}{\partial m_j}\right] = \frac{2\,R\,T}{m_j} + R\,T\,\left[\frac{\partial\ln\left(\gamma_{\pm}\right)}{\partial m_j}\right]$$

As for a non-ionic solute,

$$\text{limit}\,(m_j \rightarrow 0)\,\left[\frac{\partial\mu_j(aq;T;p)}{\partial m_j}\right] = \infty$$

From the Gibbs - Helmholtz equation and equation (v),

$$H_j(aq;T;p) = H_j^0(aq;T;p) + 2\,R\,T^2\,S_H\,\left(m_j/m^0\right)^{1/2}$$

where

$$S_H = (\partial S_\gamma/\partial T)_p$$

Further,

$$[\partial H_j(aq;T;p)/\partial m_j] = R\,T^2\,S_H\,/\left(m_j\,m^0\right)^{1/2} + 2\,R\,T^2\,\left(m_j/m^0\right)^{1/2}\,(\partial S_H/\partial m_j)$$

Thus the gradient of a plot of $H_j(aq)$ against m_j has infinite slope in the $\text{limit}\,(m_j \to 0)$. A similar pattern emerges in the case of partial molar volumes of the salt [2].

A similar analysis can be undertaken with respect to the partial molar properties of the solvent and apparent molar thermodynamic properties of salts and neutral solutes.

Footnote

[1] M. Spiro, Educ. Chem.,1966,**3**,139.

[2] J. E. Garrod and T. H. Herrington, J. Chem. Educ.,1969,**46**,165.

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1.14.34: Extent of Reaction- Chemical Equilibrium- Dependence on Temperature and Pressure- Laws of Moderation

A given chemical equilibrium exists within a closed system at defined temperature and pressure. The system is perturbed to a neighbouring equilibrium state by a change in pressure at fixed temperature and by change in temperature at fixed pressure. We take these two perturbations in turn, recognising that in both original and perturbed states the affinity for spontaneous chemical reaction is zero.

The differential change in composition resulting from a change in pressure is given by Equation 1.14.34.1.

$$\left(\frac{\partial \xi}{\partial \mathrm{p}}\right)_{\mathrm{T,A}} = \frac{(\partial \mathrm{V}/\partial \xi)_{\mathrm{T,p}}}{(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}}} \tag{1.14.34.1}$$

But at equilibrium $(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}} < 0$ where ξ is taken as positive in the direction 'reactants to products'. The property $(\partial \mathrm{V}/\partial \xi)_{\mathrm{T_p}}$ is the volume of reaction $\Delta_{\mathrm{r}}\mathrm{V}$. Thus if $\Delta_{\mathrm{r}}\mathrm{V} > 0$, an increase in pressure produces a shift in the equilibrium position to favour reactants. A shift favouring products results if $\Delta_{\mathrm{r}}\mathrm{V} < 0$.

The differential change in composition resulting from a change in temperature is given by Equation 1.14.34.2.

$$\left(\frac{\partial \xi}{\partial \mathrm{T}}\right)_{\mathrm{p,A}} = -\frac{[\mathrm{A} + (\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}]}{\mathrm{T}\,(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}}} \tag{1.14.34.2}$$

At equilibrium A is zero and $(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}} < 0$. Then an increase in temperature (at fixed p) for an exothermic reaction (where $\Delta_{\mathrm{r}}\mathrm{H} < 0$) results in a shift in the equilibrium position to favor reactants. An opposite shift results if the reaction is endothermic, i.e. $\Delta_{\mathrm{r}}\mathrm{H} > 0$.

The conclusions described above fall under the general heading 'Theorems of Moderation'. One of the authors (MJB) was taught that the outcome was 'Nature's Law of Cussedness' [= obstinacy]. An exothermic reaction generates heat which might raise the temperature of the system so the system responds, when the temperature is raised by a chemist, by shifting the equilibrium in the direction for which the process is endothermic. This line of argument is not good thermodynamics but makes the point. In the context of 'obstinacy', note the switch in sign on going from equations (c) to (d). The Principle of Le Chatelier and Braun is a theorem of moderation [1,2].

Footnotes

[1] J. de Heer, J. Chem. Educ. 1957,**34**,375.

[2] J. de Heer, Phenomenological Thermodynamics with Applications to Chemistry, Prentice-Hall, Englewood Cliffs, N.J., 1986, chapter 20.

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1.14.34: Internal Pressure

According to the Thermodynamic Equation of State,

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - \mathrm{p}$$

The partial differential $(\partial \mathrm{U}/\partial \mathrm{V})_{\mathrm{T}}$ (with units, Nm^{-2}) is the internal pressure π_{int}.

$$\pi_{\mathrm{int}} = \mathrm{T}\,\beta_{\mathrm{V}} - \mathrm{p}$$

\(\pi_{\mathrm{int}}\) describes the sensitivity of energy U to a change in volume. A high \(\phi_{\mathrm{int}}\) implies strong inter-molecular cohesion [1-8]. For many liquids, $\mathrm{T}\,\beta_{\mathrm{V}} >> \mathrm{p}$ such that

$$(\partial \mathrm{U}/\partial \mathrm{V})_{\mathrm{T}} \cong \mathrm{T}\,\beta_{\mathrm{V}}$$

$\mathrm{T}\,\beta_{\mathrm{V}}$ is sometimes called the thermal pressure. By definition, for n moles of a perfect gas,

$$\mathrm{p}\,\mathrm{V} = \mathrm{n}\,\mathrm{R}\,\mathrm{T}$$

Then

$$\mathrm{V}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \mathrm{n}\,\mathrm{R}$$

Or,

$$\mathrm{T}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \mathrm{n}\,\mathrm{R}\,\mathrm{T}/\mathrm{V} = \mathrm{p}$$

From equation (a), for a perfect gas, $\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$ is zero.

The internal pressure for water(ℓ) presents an interesting puzzle [9]. From equations (a) and (c), it follows that [1]

$$\pi_{\mathrm{int}} = \mathrm{T}\left(\frac{\alpha_{\mathrm{p}}}{\kappa_{\mathrm{T}}}\right) - \mathrm{p}$$

But at the temperature of maximum density (TMD), α_p is zero. So near the TMD, \(\pi_{\mathrm{int}}\) is zero. We understand this pattern if we think about hydrogen bonding. In order to form a strong hydrogen bond between two neighboring water molecules the O-H---O link has to be close to if not actually linear. In other words the molar volume for water(ℓ) is larger than the molar volume of a system comprising close-packed water molecules. Consequently hydrogen bonding has a strong 'repulsive' component to intermolecular interaction. However once formed hydrogen bonding has a strong cohesive contribution to intermolecular forces. Hence for water between 273 and 298 K cohesive and repulsive components of hydrogen bonding play almost competitive roles.

Footnotes

[1] Using a calculus operation, $\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T$ For equilibrium properties,

$$\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \frac{\alpha_{\mathrm{p}}}{\kappa_{\mathrm{T}}}$$

[2] Some authors use the term 'isochoric thermal pressure coefficient' for the property, $\left(\frac{\partial p}{\partial T}\right)_V$

[3] For details of original proposals concerning internal pressures see the following references.

i. W. Westwater, H. W. Frantz and J. H. Hildebrand, Phys.Rev.,1928, 31,135.
ii. J. H. Hildebrand, Phys.Rev.,1929,34,649 and 984.
iii. See also S. E. Wood, J.Phys.Chem.,1962,66, 600.

[4] Internal pressures are quoted in the literature using many units. Here we use $\mathrm{Nm^{-2}}$. We list some internal pressures and relative permitivities at 298.15 K.

liquid	\(\varepsilon_{\mathrm{r}}\(	$\pi_{\mathrm{int}}/10^5$ $\mathrm{Nm^{-2}}$
water	78.5	1715
methanol	32.63	2849
ethanol	24.30	2908
propanone	20.7	3368
diethyl ether	4.3	2635
tetrachloromethane	2.24	3447
dioxan	2.2	4991

The above details are taken from M. R. J. Dack, J.Chem.Educ.,1974,**51**,231;see also

i. Aust. J. Chem.,1976, **29**,771 and 779.
ii. D. D. MacDonald and J. B. Hyne, Can.J.Chem.,1971, **49**,2636

[5] For a discussion of effects of solvents on rates of chemical reactions with reference to internal pressures, see

a. K. Colter and M. L. Clemens, J.Phys.Chem.,1964,**68**,651.
b. A. P. Stefani, J. Am. Chem.Soc.,1968,**90**,1694.

[6] For comments on solvent polarity and internal pressures see J. E. Gordon, J. Phys. Chem.,1966,**70**,2413.

[7] For comments on internal pressures of binary aqueous mixtures see D. D. Macdonald, Can. J Chem.,1976,**54**,3559; and references therein.

[8] For comments on effect of internal pressure on conformational equilibria see R. J. Ouellette and S. H. Williams, J. Am. Chem.Soc.,1971,**93**,466.

[9] For details concerning the dependence of internal pressure of water and $\mathrm{D_2O}$, see M. J. Blandamer, J. Burgess and A.W.Hakin, J. Chem. Soc. Faraday Trans. 1, 1987, **83**, 1783.

[10] For comments on the calculation of excess internal pressures for binary liquid mixtures using equation (h) see W. Marczak, Phys.Chem.Chem.Phys.,2002,**4**,1889.

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1.14.35: Internal Pressure: Liquid Mixtures: Excess Property

The thermodynamic equation of state takes the form shown in equation (a).

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - \mathrm{p}$$

The partial differential $(\partial \mathrm{U}/\partial \mathrm{V})_{\mathrm{T}}$ is the internal pressure, π_{int} (with units, Nm^{-2}). A calculus operation relates three interesting partial derivatives in the context of $\mathrm{p}-\mathrm{V}-\mathrm{T}$ properties; equation (b).

$$\left(\frac{\partial p}{\partial T}\right)_{V} = -\left(\frac{\partial V}{\partial T}\right)_{p}\left(\frac{\partial p}{\partial V}\right)_{T}$$

For a given liquid at defined T and p, the isobaric (equilibrium) thermal expansion, $\mathrm{E_p}$ equals $(\partial \mathrm{V}/\partial \mathrm{T})_{\mathrm{p}}$. The isothermal (equilibrium) compression $\mathrm{K_T}$ is defined by $-(\partial \mathrm{V}/\partial \mathrm{p})_{\mathrm{T}}$. According to equations (a) and (b), π_{int} is given by equation (c).

$$\pi_{\mathrm{int}} = (\mathrm{T}\,\mathrm{E_p}/\mathrm{K_T}) - \mathrm{p}$$

For the purpose of the analysis described here, equation (c) describes the equilibrium molar properties of a given binary liquid mixture at temperature T and pressure p. The internal pressure is a non-Gibbsian property of a liquid. Nevertheless it is interesting to compare internal pressures of real and the corresponding ideal binary liquid mixture [1]. In other words we require an equation for the internal pressure of binary liquid mixture $\pi^{\mathrm{id}}_{\mathrm{int}}$ having thermodynamic properties which are ideal. Marczak[1] uses equation (c) in which the corresponding molar properties of the mixture, mole fraction composition $\mathrm{x_2}$, $\mathrm{E^{id}_{pm}}(\mathrm{x_2})$ and $\mathrm{K^{id}_{Tm}}(\mathrm{x_2})$ are given by the mole fraction weighted properties of the pure liquids.

$$\mathrm{E^{id}_{pm}}(\mathrm{x_2}) = \sum_{\mathrm{i}=1}^{\mathrm{i}=2} \mathrm{x_i}\,\mathrm{E^{*}_{pi}}(\ell)$$

$$\mathrm{K^{id}_{Tm}}(\mathrm{x_2}) = \sum_{\mathrm{i}=1}^{\mathrm{i}=2} \mathrm{x_i}\,\mathrm{K^{*}_{Ti}}(\ell)$$

Equations (d) and (e) can be generalised to multi-component liquid mixtures. From equation (c) for a binary liquid mixture having thermodynamic properties which are ideal, the internal pressure $\pi^{\mathrm{id}}_{\mathrm{int}}(\mathrm{x_2})$ is given by equation (f).

$$\pi^{\mathrm{id}}_{\mathrm{int}}(\mathrm{x_2}) = \mathrm{T}\,\frac{\mathrm{E^{id}_{pm}}(\mathrm{x_2})}{\mathrm{K^{id}_{Tm}}(\mathrm{x_2})} - \mathrm{p}$$

Or using equations (d) and (e),

$$\pi^{\mathrm{id}}_{\mathrm{int}}(\mathrm{x_2}) = \frac{\sum_{\mathrm{i}=1}^{\mathrm{i}=2}\ \mathrm{T}\,\mathrm{x_i}\,\mathrm{E^{*}_{pi}}(\ell)}{\sum_{\mathrm{i}=1}^{\mathrm{i}=2}\mathrm{x_i}\,\mathrm{K^{*}_{Ti}}(\ell)} - \mathrm{p}$$

Equation (g) is re-written to establish $\pi^{*}_{\mathrm{int,i}}(\ell)$ as a term on the r.h.s. of the latter equation for $\pi^{\mathrm{id}}_{\mathrm{int}}(\mathrm{x_2})$.

$$\pi^{\mathrm{id}}_{\mathrm{int}}(\mathrm{x_2}) = -\mathrm{p} + \frac{\sum_{\mathrm{i}=1}^{\mathrm{i}=2}\ \mathrm{T}\,\mathrm{x_i}\,\mathrm{E^{*}_{pi}}(\ell)\,\mathrm{K^{*}_{Ti}}(\ell)/\mathrm{K^{*}_{Ti}}(\ell)}{\sum_{\mathrm{i}=1}^{\mathrm{i}=2}\mathrm{x_i}\,\mathrm{K^{*}_{Ti}}(\ell)}$$

But according to equation (c) , for the pure liquid–i,

$$\pi^{*}_{\mathrm{im,i}}(\ell) + \mathrm{p} = \mathrm{T}\,\mathrm{E^{*}_{pi}}(\ell)/\mathrm{K^{*}_{Ti}}(\ell)$$

Hence from equation (h),

$$\pi^{\mathrm{id}}_{\mathrm{int}}(\mathrm{x_2}) = -\mathrm{p} + \frac{\sum_{\mathrm{i}=1}^{\mathrm{i}=2}\mathrm{x_i}\ \left[\pi^{*}_{\mathrm{int,i}}(\ell) + \mathrm{p}\right]\ \mathrm{K^{*}_{T_i}}(\ell)}{\sum_{\mathrm{i}=1}^{\mathrm{i}=2}\mathrm{x_i}\,\mathrm{K_{Ti^{*}}}(\ell)}$$

In other words,

$$\pi^{id}_{idt}\,(x_2) = -\,p + \frac{x_1\,\pi^*_{int11}(\ell)\,K^*_{T1}(\ell)}{\sum_{i=1}^{i=2} x_i\,K^*_{Ti}(\ell)} + \frac{x_1\,p\,K^*_{T1}(\ell)}{\sum^*_{i=2} x_i\,K^*_{Ti}(\ell)} + \frac{x_2\,\pi^*_{int,2}(\ell)\,K^*_{T2}(\ell)}{\sum_{i=1}^{i=2} x_i\,K^*_{Ti}(\ell)} + \frac{x_2\,p\,K^*_{T2}(\ell)}{\sum_{i=1}^{i=2} x_i\,K^*_{Ti}(\ell)}$$

Hence,

$$\pi^{id}_{int}\,(x_2) = \frac{\sum_{i=1}^{i=2} x_i\,\pi^*_{int,i}(\ell)\,K^*_{Ti}(\ell)}{\sum_{i=1}^{i=2} x_i\,K^*_{Ti}(\ell)}$$

By definition [1], for liquid component k,

$$\Psi_k = \frac{x_k\,K^*_{Tk}(\ell)}{\sum x_i\,K^*_{Ti}(\ell)}$$

In other words,

$$\pi^{id}_{int}\,(x_2) = \sum_{i=1}^{i=2} \psi_i\,\pi^*_{int,i}(\ell)$$

The corresponding excess internal pressure at mole fraction x_2,

$$\pi^{E}_{int}\,(x_2)$$

is defined by equation (o).

$$\pi^{E}_{int}\,(x_2) = \pi_{int}\,(x_2) - \sum_{i=1}^{i=2} \psi_i\,\pi^*_{int,i}(\ell)$$

Marczak [1] reports $\pi^{E}_{int}\ (X_2)$ as a function of mole fraction x_2 for two binary liquid mixtures at $298.15\ K$;

a. methanol + propan-1-ol, and
b. tribromomethane + n-octane.

Footnotes

[1] W. Marczak, Phys. Chem. Chem. Phys.2002,**4**,1889.

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1.14.36: Irreversible Thermodynamics

According to the Second Law of Thermodynamics, the change in entropy dS is related to the affinity for spontaneous change A using equation (a).

$$\mathrm{dS} = (\mathrm{q}/\mathrm{T}) + (\mathrm{A}/\mathrm{T})\,\mathrm{d}\xi; \quad \mathrm{A}\,\mathrm{d}\xi \geq 0$$

In these terms chemists usually have in mind a chemical reaction driven by the affinity A for spontaneous chemical reaction producing extent of reaction $\mathrm{d}\xi$. We generalize the law in the following terms.

$$\mathrm{dS} = (\mathrm{q}/\mathrm{T}) + \mathrm{d_iS}; \quad \mathrm{d_iS} \geq 0$$

$\mathrm{d_iS}$ is the change in entropy of the system by virtue of spontaneous processes in the system. Comparison of equations (a) and (b) yields the following equation.

$$\mathrm{T}\,\mathrm{d_iS} = \mathrm{A}\,\mathrm{d}\xi \geq 0$$

We introduce two new terms. A quantity $\mathrm{P[S]}$ describes the rate of entropy production within the system; a quantity $\sigma[\mathrm{S}]$ describes the corresponding rate of entropy production in unit volume of the system.

$$\mathrm{P[S]} = \mathrm{d_iS}/\mathrm{dt} = \int_{\mathrm{V}} \sigma[\mathrm{S}]\,\mathrm{dV} \geq 0$$

We combine equations (c) and (d).

$$\mathrm{P[S]} = \frac{\mathrm{d_iS}}{\mathrm{dt}} = \frac{\mathrm{A}}{\mathrm{T}}\frac{\mathrm{d}\xi}{\mathrm{dt}} \geq 0$$

But if dn_j is the change in amount of chemical substance j in the system, $\mathrm{dnj_j} = \mathrm{v_j}\,\mathrm{d}\xi$. Then,

$$P[S] = \frac{d_iS}{dt} = \frac{A}{T}\frac{1}{v_j}\frac{dn_j}{dt} \geq 0$$

We develop this equation into a form which has wider significance. We assume that the system is homogeneous such that for a system volume V,

$$\sigma[S] = P[S]/V$$

Then

$$\sigma[\mathrm{S}] = \frac{1}{\mathrm{V}}\frac{\mathrm{d_iS}}{\mathrm{dt}} = \frac{\mathrm{A}}{\mathrm{T}}\frac{1}{\mathrm{v_j}}\frac{1}{\mathrm{V}}\frac{\mathrm{dn_j}}{\mathrm{dt}} \geq 0$$

But the concentration of chemical substance j, $\mathrm{c_j} = \mathrm{n_j}/\mathrm{V}$. Then, $\mathrm{dc_j} = \mathrm{dn_j}/\mathrm{V}$. Hence from equation (h),

$$\sigma[S] = \frac{\mathrm{A}}{\mathrm{T}}\frac{1}{\mathrm{v_j}}\frac{\mathrm{dc_j}}{\mathrm{dt}} \geq 0$$

The quantity $(1/v_j)\ dc_j/dt$ describes the change in composition of the system, the **flow** of the system from reactants to products. In these terms we identify a chemical flow, $\mathrm{J_{ch}}$.

$$\mathrm{J_{ch}} = (\mathrm{l}/\mathrm{v_j})\ \mathrm{dc_j}/\mathrm{dt}$$

Then,

$$\sigma[S] = (A/T)\,J_{ch} \geq 0$$

Or,

$$\mathrm{T}\,\sigma[\mathrm{S}] = \mathrm{A}\,\mathrm{J_{ch}} \geq 0$$

The latter equation has an interesting feature; $\mathrm{T}\,\sigma[\mathrm{S}]$ is given by the product of the affinity for spontaneous chemical reaction (the driving force) and the accompanying flow. Indeed $\mathrm{T}\,\sigma[\mathrm{S}]$ is related to the rate of entropy production in the system. Thermodynamics

takes us no further. We make an extrathermodynamic leap and suggest that the flow is proportional to the force; i.e. the stronger the driving force the more rapid the chemical flow from reactants to products.

In general terms phenomenological equations start out from the basis of a linear model described by a phenomenological law of the general form, $\mathrm{J} = \mathrm{L} \backslash (\mathrm{X}$ where J is the flow and X is the conjugate force such that the product $\mathrm{J}\ \mathrm{X}$ yields the rate of entropy production. These laws are based on experiment. Many such phenomenological laws have been proposed. Some examples are listed below.

1. Phenomenon--- Electrical Conductivity Law: Ohm's Law (discovered 1826)
   $\mathrm{I} = \mathrm{L}\,\mathrm{V}$ where $\mathrm{L} =$ conductance; resistance $\mathrm{R} = 1/\mathrm{L}$.
2. Phenomenon--- Diffusion Law: Fick's Law discovered by Adolf Fick 1855
   $\mathrm{J_j} = \mathrm{D}\ (-\mathrm{d}\mu_\mathrm{j}/\mathrm{dx})$
3. Phenomenon— Thermal conductivity Law : Fourier's Law (1822)
   $\mathrm{J_q} = \lambda\,(-\mathrm{dT}/\mathrm{dx})$ $\lambda =$ thermal conductivity
4. Phenomenon—Chemical reaction If the patterns described above were followed we might write,
   $J_{ch} = L\,A$

In 1890 Nernst suggested this approach to chemical kinetics. Unfortunately chemists have no method for measuring the affinity; there is no affinity meter. Instead chemists use the Law of Mass Action.

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1.14.37: Irreversible Thermodynamics: Onsager Phenomenological Equations

The major thrust of the account presented in these Topics concerns reversible processes in which system and surroundings are in thermodynamic equilibrium. When attention turns to non-equilibrium processes, the thermodynamic treatment is necessarily more complicated [1-5]. Here we examine several aspects of irreversible thermodynamics for near equilibrium in open systems[1]. In other words there is a strong 'communication' between system and surroundings. With increasing displacement of a given system from equilibrium the thermodynamic analysis becomes more complicated and controversial [2-5]. Here we confine attention to processes in near-equilibrium states [6]. The key assumption is that equations describing relationships between thermodynamic properties are valid for small elemental volumes, the concept of local equilibrium. Hence we can in a description of a given system identify the energy per unit volume and the entropy per unit volume in the context respectively of the first and second laws of thermodynamics.

With respect to a small volume dv of a given system the change in entropy ds is given by the change in entropy $\mathrm{d_i s}$ by virtue of processes within a small volume dv and by virtue of exchange with the rest of the system, des. The rate of change of $\mathrm{d_i s}$, namely $\mathrm{d_i s/dt}$ is the local entropy production and is determined by the following condition.

$$\sigma \equiv \mathrm{d_i s/dt} \geq 0$$

Phenomenological Laws

For systems close to thermodynamic equilibrium, the entropy production per unit volume σ can be expressed as the sum of products of forces $\mathrm{X_k}$ and conjugate flows, $\mathrm{J_k}$. Thus for k flows and forces,

$$\sigma = \sum_{\mathrm{k}} \mathrm{X_k\, J_k}$$

The condition 'conjugate' is important in the sense that for each flow J_k there is a conjugate force X_k. For near equilibrium systems a given flow is a linear function of the conjugate force, X_k. Then,

$$\mathrm{J_k} = \sum_{\mathrm{j}} \mathrm{L_{kj}\, X_k}$$

The property $\mathrm{L_{kj}}$ is a phenomenological coefficient describing the dynamic flow and conjugate force.

In simple systems there is only one flow and one force such that the flow is directly proportional to the force. A classic example is Ohm's law which can be written in the following form.

$$\mathrm{I} = (1/\mathrm{R})\, \mathrm{V}$$

Thus I is the electric current, the rate of flow of electric charge for a system where the driving force is the electric potential gradient V. The relevant property of the system under consideration is the resistance R or, preferably, its conductance $\mathrm{L}(= 1/\backslash(\mathrm{R})$.

A similar phenomenological law is Fick's Law of diffusion relating the rate of diffusion of chemical substance j, J_j to the concentration gradient $\mathrm{dc}_j/\mathrm{dx}$ where D_j describes the property of diffusion. Thus

$$\mathrm{J_j} = \mathrm{D_j}\ (\mathrm{dc_j/dx})$$

The Law of Mass Action is a similar phenomenological law. In other words throughout chemistry (and indeed all sciences) there are phenomenological laws which do not, for example, follow from the first and second laws of thermodynamics.

Onsager Equations

Following on a proposal by Lord Rayleigh relating to mechanical properties, in 1931 Onsager [7] extended the ideas discussed above to include all forces and flows. For a system involving two flows and forces we may write the following two equations to describe near –equilibrium systems.

$$\mathrm{J_1} = \mathrm{L_{11}\, X_1} + \mathrm{L_{12}\, X_2}$$

$$\mathrm{J_2} = \mathrm{L_{21}\, X_1} + \mathrm{L_{22}\, X_2}$$

This formulation recognises that force X_2 may also produce a coupled flow J_1. In each case the products $L_{11}\,X_1,\ L_{12}\,X_2,\ L_{21}\,X_1$ and $L_{22}\,X_2$ involve conjugate flows and forces such that the product, $J_i\,X_i$ has the dimension of the rate of entropy production. The cross terms L_{12} and L_{21} are the coupling coefficients such that for example, force X2 produces flow J1.

Onsager's Law

The key theoretical advance made by Onsager was to show that for near-equilibrium states the matrix of coefficients is symmetric. Then, for example,[8]

$$L_{12} = L_{21}$$

The point can be developed by considering a system involving two flows and two forces. According to equation (b)

$$\sigma = J_1\,X_1 + J_2\,X_2$$

Hence from equations (f) and (g)

$$\sigma = L_{11}\,X_1^2 + (L_{12} + L_{21})\ X_1\,X_2 + L_{22}\,X_2^2 > 0$$

It also follows that [8]

$$L_{11}\,X_1^2 \geq 0 \quad ; \quad L_{22}\,X_2^2 \geq 0$$

And,

$$L_{11}\,L_{22} \geq L_{12}^2$$

Electrokinetic Phenomena[1]

These phenomena illustrate the application of the equations discussed above. A membrane separates two salt solutions; an electric potential E and a pressure gradient are applied across the membrane. There are two flows;

i. solution flows through the membrane, described as a volume flow;
ii. an electric current.

The dynamics of the system are described by the dissipation function ϕ given by equation (m), the sum of products of flows and forces.

$$\phi = J_V\,\Delta p + I\,E$$

The dynamics of the system are described by two dynamic equations,

$$J_V = L_{11}\,\Delta p + L_{12}\,E$$

$$I = L_{21}\,\Delta p + L_{22}\,E$$

Onsager's law requires that,

$$L_{12} = L_{21}$$

In an experiment we set E at zero. Then

$$L_{11} = \left(\frac{J_v}{\Delta p}\right)_{E=0}$$

However the electric current is not zero. According to equation (o),

$$I = L_{21}\,\Delta p$$

In other words, there is a coupled flow of ions. Katchalsky and Curran [1] discuss numerous experiments which illustrate this type of coupling of flows and forces.

Footnotes

[1] A. Katchalsky and P. F. Curran, Non-Equilibrium Thermodynamics in Biophysics, Harvard University Press, 1965.

[2] P. Glandsorff and I. Prigogine, Thermodynamics of Structure Stability and Fluctuations, Wiley-Interscience, London,1971.

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[4] P Gray and S. K. Scott, Chemical Oscillations and Instabilities, Oxford,1990.

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[6] D. Kondepudi and I. Prigogine, Modern Thermodynamics, Wiley, New York, 1998.

[7] L. Onsager, Phys. Rev.,1931,**38**,2265.

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1.14.38: Joule-Thomson Coefficient

An important property of a given gas is its Joule-Thomson coefficient [1-3]. These coefficients are important from two standpoints;

i. intermolecular interaction, and
ii. liquefaction of gases.

A given closed system contains one mole of gaseous chemical substance j at temperature T and pressure p. The molar enthalpy of the gas $\mathrm{H_j}$ describes its molar enthalpy defined by equation (a).

$$\mathrm{H_j = H_j[T, p]}$$

Then,

$$\mathrm{dH_j} = \left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{T}}\right)_{\mathrm{p}} \mathrm{dT} + \left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{p}}\right)_{\mathrm{T}} \mathrm{dp}$$

Hence at constant enthalpy, H,

$$\left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{T}}\right)_{\mathrm{p}} \mathrm{dT} = -\left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{p}}\right)_{\mathrm{T}} \mathrm{dp}$$

Or,

$$\left(\frac{\partial T}{\partial p}\right)_{H} = -\left(\frac{\partial H_{\mathrm{j}}}{\partial p}\right)_{T} \left(\frac{\partial T}{\partial H_j}\right)_{p}$$

The Joule-Thomson coefficient for gas j, Extra close brace or missing open brace is defined by equation (e).

$$\mu_{\mathrm{j}} = \left(\frac{\partial T}{\partial p}\right)_{\mathrm{H(j)}}$$

For all gases (except helium and hydrogen) at $298\ \mathrm{K}$ and moderate pressures \(\mu_{\mathrm{j}} > 0\). At room temperature and ambient pressure, μ_{j} is $0.002\ \mathrm{KPa^{-1}}$ for nitrogen and $0.025\ \mathrm{KPa^{-1}}$ for 2,2-dimethylpropane [3].

Further the isobaric heat capacity for chemical substance j is defined by equation (f).

$$\mathrm{C_{pj}} = \left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

Hence from equations (d), (e) and (f),

$$\mu_{\mathrm{j}} = -\frac{(\partial \mathrm{H}/\partial \mathrm{p})_{\mathrm{T}}}{\mathrm{C_{pj}}}$$

Then,

$$\left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = -\mu_{\mathrm{j}}\, \mathrm{C_{pj}}$$

Equation (h) marks an important stage in the analysis. For example, $\mathrm{C_{pj}} > 0$. From the definition of enthalpy $\mathrm{H_j}$,

$$\mathrm{U_j = H_j - p\, V_j}$$

Equation (i) is differentiated with respect to $\mathrm{V_j} at fixed \(\mathrm{T}$. Thus,

\[

$$\left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}} = \left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}} - \mathrm{V_j}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}} - \mathrm{p}$$

Or,

$$\left(\frac{\partial U_j}{\partial V_j}\right)_{T} = \left(\frac{\partial p}{\partial V_j}\right)_{T}\left[\left(\frac{\partial H_j}{\partial V_j}\right)_{T}\left(\frac{\partial V_j}{\partial p}\right)_{T} - V_j\right] - p$$

Then,

$$\left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}} = \left(\frac{\partial \mathrm{p}}{\partial \mathrm{V_j}}\right)_{T}\left[\left(\frac{\partial \mathrm{H_j}}{\partial \mathrm{p}}\right)_{\mathrm{T}} - \mathrm{V_j}\right] - \mathrm{p}$$

Using equation (h),

$$\left(\frac{\partial U_j}{\partial V_j}\right)_T = -\left(\frac{\partial p}{\partial V_j}\right)_T [\mu_j C_{pj} + V_j] - p$$

An important application of equation (m) concerns the case where chemical substance j is a perfect gas. In this case,

$$\mathrm{p\,V_j = R\,T}$$

Or,

$$\mathrm{p = R\,T\,\frac{1}{V_j}}$$

Hence,

$$\left(\frac{\partial p}{\partial V_j}\right)_T = -RT\frac{1}{V_j^2} = -\frac{p}{V_j}$$

Then from equation (m),

$$\left(\frac{\partial U_j}{\partial V_j}\right)_T = \frac{p}{V_j}\,[\mu_j C_{pj} + V_j] - p$$

Or,

$$\left(\frac{\partial U_j}{\partial V_j}\right)_T = \frac{p\,\mu_j C_{pj}}{V_j}$$

But

$$\mathrm{limit(p \to 0)}\frac{\mathrm{p}\,\mu_{\mathrm{j}}\,\mathrm{C_{pj}}}{\mathrm{V_j}} = 0$$

Then

$$\mathrm{limit(p \to 0)}\left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}} = 0$$

A definition of a perfect gas is that $\left(\frac{\partial \mathrm{U_j}}{\partial \mathrm{V_j}}\right)_{\mathrm{T}}$ is zero. Then all real gases are perfect in the $\mathrm{limit(p \to 0)}$.

Footnotes

[1] James Prescott Joule(12818-1889) William Thomson (1824-1907); Later Lord Kelvin Some authors refer to the Joule-Thomson coefficient; e.g. E. B. Smith, Basic Chemical Thermodynamics, Clarendon Press, Oxford, 1982, 3rd. edn., page 119. Other authors refer to the Joule –Kelvin Effect; e.g. E. F. Caldin, Chemical Thermodynamics, Clarendon Press, Oxford, 1958,page 81. Other authors refer to either the Joule-Thomson or Joule-Kelvin Effect; e.g. M. H. Everdell, Introduction to Chemical Thermodynamics, English Universities Press, London 1965, page 57.

[2] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London 1979, page 94.

[3] Benjamin Thompson (1753-1814); later Count von Rumford, married Lavoisier's widow.

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1.14.39: Kinetic Salt Effects

The chemical potential of a given solute j in an aqueous solution is related to the concentration $\mathrm{c_j}$ using equation (a) where $\mathrm{c_r}$ is a reference concentration, $1\ \mathrm{moldm^{-3}}$, and yj is the solute activity coefficient.

$$\mu_{\mathrm{j}}(\mathrm{aq}) = \mu_{\mathrm{j}}^{0}\left(\mathrm{c_j} = 1\ \mathrm{moldm^{-3}}; \mathrm{aq}; \mathrm{id}\right) + \mathrm{R\,T\ ln}\left(\mathrm{c_j\,y_j/c_r}\right)$$

By definition, at all T and p,

$$\mathrm{limit}\left(\mathrm{c_j} \to 0\right)\mathrm{y_j} = 1.0$$

In the application of equation (a) to the rates of chemical reactions in solution, transition state theory [1] is used. In the case of a second order bimolecular reaction involving solutes $\mathrm{X(aq)}$ and $\mathrm{Y(aq)}$, the reaction proceeds as described by equation (c).

$$\mathrm{X(aq) + Y(aq) \Longleftrightarrow TS^{\neq} \to\ products}$$

An equilibrium between reactants and transition state, $\mathrm{TS^{\neq}}$ is described by an equilibrium constant $\mathrm{K^{\neq}}$. Hence,

$$\Delta^{\neq}\mathrm{G^0} = -\mathrm{R\,T\ ln}\left(\mathrm{K^{\neq}}\right) = \mu_{\neq}^{0}(\mathrm{aq}) - \mu_{\mathrm{X}}^{0}(\mathrm{aq}) - \mu_{\mathrm{Y}}^{0}(\mathrm{aq})$$

At equilibrium,

$$\mu^{\mathrm{eq}}(\mathrm{X;aq}) + \mu^{\mathrm{eq}}(\mathrm{Y;aq}) = \mu^{\mathrm{eq}}(\mathrm{TS;aq})$$

Using equation (a),

$$\mathrm{K^{\neq}} = \frac{\mathrm{c^{\neq}(aq)\,y^{\neq}(aq)\,c_r}}{\mathrm{c_x^{eq}(aq)\,y_X(aq)\,c_Y^{eq}(aq)\,y_Y(aq)}}$$

According to TS theory [1] rate constant k is related to $\mathrm{K^{\neq}}$ using equation (g) where κ is a transmission coefficient, customarily set to unity. Then,

$$\mathrm{k = K\,(k\,T/h)\,K^{\neq}\,y_X(aq)\,y_Y(aq)/y_{\neq}(aq)}$$

In the event that the thermodynamic properties of the aqueous solution are ideal, equation (g) simplifies to equation (h).

$$\mathrm{k(id) = \kappa\,(k\,T/h)\,K^{\neq}}$$

For a real system,

$$\mathrm{k = k(id)\,y_X(aq)\,y_Y(aq)/y_{\neq}(aq)}$$

The Bronsted-Bjerrum analysis concerns rates of chemical reaction between ions having electric charges, $\mathrm{z_x\ e}$ and $\mathrm{z_y\ e}$ where the transition state has charge z · e ≠ (z e z e) X Y = · + · .

In most applications, the activity coefficients are related to the ionic strength of the solution using the Debye - Huckel Limiting Law. For reactant j,

$$\mathrm{ln\left(y_j\right) = -S_Y\,z_j^2\ \left(I/m^0\right)^{1/2}}$$

Then,

$$\mathrm{ln(k) = ln(k(id)) + ln\left(y_X\right) + ln\left(y_Y\right) - ln\left(y_z\right)}$$

$$\mathrm{ln(k) = ln(k(id)) - S_y\ \left(I/m^0\right)^{1/2}\ \left[z_X^2 + z_Y^2 - \left(z_X + z_Y\right)^2\right]}$$

Or,

$$\mathrm{ln(k) - ln(k(id)) = S_y\ \left(I/m^0\right)^{1/2}\ [2\,z_X\,Z_Y]}$$

Equation (m) forms the basis of the classic and oft-quoted plot of $\mathrm{[ln(k) - ln(k(id))]}$ against $\left(\mathrm{I/m^0}\right)^{1/2}$ in which the slope is determined by the product of charge numbers, $\mathrm{z_x\,z_y}$; [1;see Footnote (1), page 429].

An interesting feature was noted by Rosseinsky [2]. Equation (m) can be written in a quite general form for a reaction involving n ions. Then,

$$\ln(k) - \ln(k(id)) = S_y \left(I/m^0\right)^{1/2} \sum_i^n \sum_j^n z_i z_j \quad (i \neq j)$$

For chemical reaction involving cations and anions , cases can arise where the double sum in equation(n) is zero. Hence the rate constant will be independent of ionic strength. Rosseinsky cites the following reaction as a case in point [3].

$$2Mn^{2+}(aq) + MnO_4^-(aq) \rightarrow Mn_3O_4^{3+}$$

Footnotes

[1] S. A. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941, pp. 427-429.

[2] D. R. Rosseinsky, J. Chem. Phys.,1968,**48**, 4806.

[3] D. R. Rosseinsky and M. J. Nicol, Trans. Faraday Soc.,1965,**61**, 2718.

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1.14.40: Laws of Thermodynamics

A remarkable feature of the subject called thermodynamics is the extent to which it is founded on four laws: Zeroeth, First, Second and Third. These laws summarize elegantly the results of experiments. Actually these are not laws in the sense of being laid down by government or by religious doctrine. Rather the laws are **axioms**. As McGlashan notes [1] each axiom is a 'rule of the game'. These axioms refer to state variables such as temperature, pressure, energy and entropy. At this level the laws are not of immediate interest to chemists. However chemists have discovered how to 'tell' these axioms about chemical substances and chemical reactions.

The First Law invokes the concepts of energy and energy change. The law states that the energy of the universe is constant. In a realistic sense, at least for chemists, the law states that the energy of a chemical laboratory is constant. Then if the energy of system held in a reaction vessel increases, an equivalent amount of energy is lost from the rest of the laboratory. Then

$$\Delta \mathrm{U}(\text{ system }) + \Delta \mathrm{U}(\text{ surroundings }) = 0$$

The Second Law of thermodynamics invokes the concepts of entropy and entropy change. In summary the law states that heat cannot flow spontaneously from low to high temperatures. The elegant studies carried out by James Prescott Joule (1818 -1889) were crucial to the development of thermodynamics [2].

Footnotes

[1] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London 1979.

[2] L. Woodcock and L. Lue, Chem. Britain, 2001, August, p. 38.

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1.14.41: Lewisian Variables

A given liquid mixture is prepared using n_1 moles of liquid 1 and n_2 moles of liquid 2. If the thermodynamic properties of the liquid mixture are ideal the volume of the mixture is given by the sum of products of amounts and molar volumes (at the same T and p); equation (a).

$$\mathrm{V}(\mathrm{mix};\mathrm{id}) = \mathrm{n}_1\,\mathrm{V}_1^*(\ell) + \mathrm{n}_2\,\mathrm{V}_2^*(\ell)$$

If the thermodynamic properties of the mixture are not ideal, the volume of the (real) mixture is given by equation (b).

$$V(\mathrm{mix}) = \mathrm{n}_1\,\mathrm{V}_1(\mathrm{mix}) + \mathrm{n}_2\,\mathrm{V}_2(\mathrm{mix})$$

$\mathrm{V}_1(\mathrm{mix})$ and $\mathrm{V}_2(\mathrm{mix})$ are the partial molar volumes of chemical substances 1 and 2 defined by equations (c) and (d).

$$\mathrm{V}_1(\mathrm{mix}) = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{n}_1}\right)_{\mathrm{T,p,n(2)}}$$

$$\mathrm{V}_2(\mathrm{mix}) = \left(\frac{\partial V}{\partial n_2}\right)_{T,p,n(1)}$$

The similarities between equations (a) and (b) are obvious and indicate an important method for describing the extensive properties of a given system. This was the aim of G. N. Lewis who sought equations of the form show in equation (b). In general terms we identify an extensive property X of a given system such that the variable can be written in the general form shown in equation (e).

$$\mathrm{X} = \mathrm{n}_1\,\mathrm{X}_1 + \mathrm{n}_2\,\mathrm{X}_2$$

where

$$\mathrm{X}_1 = \left(\frac{\partial \mathrm{X}}{\partial \mathrm{n}_1}\right)_{\mathrm{T,p,n(2)}}$$

$$\mathrm{X}_2(\mathrm{mix}) = \left(\frac{\partial \mathrm{X}}{\partial \mathrm{n}_2}\right)_{\mathrm{T,p,n(1)}}$$

Other than the composition variables, the conditions on the partial differentials in equations (f) and (g) are intensive properties;

i. mechanical variable, pressure, and
ii. thermal variable, temperature.

Lewisian partial molar variables can be used to describe the thermodynamic energy U, entropy S and volume V together with their Legendre transforms, Helmholtz energy, enthalpy and Gibbs energy. With respect to other thermodynamic properties of a closed system, the case for identifying similar Lewisian partial molar properties has to be established. It turns out that partial molar expansions [e.g. $\mathrm{E}_{\mathrm{p}j}(\mathrm{T},\mathrm{p})$] and partial molar compressions [e.g. $\mathrm{K}_{\mathrm{T}j}(\mathrm{T},\mathrm{p})$] for chemical substance j in a closed single phase system are Lewisian but partial molar isentropic compressions are not .

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1.14.42: L'Hospital's Rule

In several important cases, analysis of thermodynamic properties of solutions (and liquid mixtures) requires consideration of a term having the general form $x\ \ln(x)$ where x is an intensive composition variable; e.g. molality, concentration or mole fraction. The accompanying analysis requires an answer to the question --- what value does the product $x\ \ln(x)$ take in the limit that x tends to zero. But $\text{limit}(x \to 0)\ln(x) = -\infty$. The thermodynamic analysis has to take account of the answer to this question. In fact most accounts assume that the answer to the above question is 'zero'. Confirmation that the latter statement is correct emerges from application of L'Hospital's Rule (G. F. A. de l'Hospital, 1661-1704, marquis de Saint-Mesme). This rule allows the evaluation of terms having indeterminate forms. Most applications of this method usually involve the ratio of two terms each being a function of x.

If $\mathrm{f(x)/F(x)}$ approaches either [0/0] or $[\infty/\infty]$ when x approaches **a**, and $\mathrm{f'(x)/F'(x)}$ [where $\mathrm{f'(x)}$ and $\mathrm{F'(x)}$ are first derivatives of $\mathrm{f(x)}$ and $\mathrm{F(x)}$] approaches a limit as x approaches **a**, then $\mathrm{f(x)/F(x)}$ approaches the same limit.

Example 1.14.42.1

If $f(x) = x^2 - 1$ and $F(x) = x - 1$

then $\frac{f(x)}{F(x)} = \frac{x^2-1}{x-1}$ and $\frac{f'(x)}{F'(x)} = \frac{2\,x^2}{1}$

then

$$\text{limit}(x \to 1)\frac{f'(x)}{F'(x)} = 2$$

Hence,

$$\text{limit}(x \to 1)\frac{f(x)}{F(x)} = 2$$

This rule can be proved using three assumptions.

i. In the neighborhood of $x = a$, $F(x) \neq 0$ if $x \neq \mathrm{a}$.
ii. $f(x)$ and $F(x)$ are continuous in the neighbourhood of $x = \mathrm{a}$ except perhaps at a.
iii. $\mathrm{f'}(x)$ and $\mathrm{F'}(x)$ exist is some neighborhood of $x = \mathrm{a}$ (except perhaps at $x = \mathrm{a}$) and do not vanish simultaneously for $x \neq \mathrm{a}$.

In the present context the terms under consideration have a different form. With reference to the term, $x\ \ln(x)$,

$$f(x) = \ln(x) \text{ and } F(x) = 1/x$$

Then $\mathrm{f'(x)} = 1/\mathrm{x}$ and $\mathrm{F'(x)} = -1/\mathrm{x}^2$.

Hence, $\mathrm{f'(x)/F'(x)} = -\mathrm{x}$.

Thus

$$\text{limit}(x \to 0)\mathrm{f'}(x)/\mathrm{F'(x)} = 0$$

Hence,

$$\text{limit}(x \to 0)x\ \ln(x) = 0$$

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1.14.43: Master Equation

Two important laws of thermodynamics describe spontaneous change in a closed system.

First Law

$$\mathrm{dU} = \mathrm{q} - \mathrm{p}\,\mathrm{dV}$$

Second Law

$$\mathrm{T}\,\mathrm{dS} = \mathrm{q} + \mathrm{A}\,\mathrm{d}\xi; \mathrm{A}\,\mathrm{d}\xi \geq 0$$

Heat q is common to these equations which we combine. The result is a very important equation.

$$\mathrm{dU} = \mathrm{T}\,\mathrm{dS} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi$$
$$\mathrm{A}\,\mathrm{d}\xi \geq 0$$

We use the description 'Master Equation'. A case can be made for the statement that chemical thermodynamics is based on this Master Equation.

The Master Equation describes the differential change in the thermodynamic energy of a closed system.

$$\mathrm{dU} = \mathrm{T}\,\mathrm{dS} - \mathrm{p}\,\mathrm{dV} - \mathrm{A}\,\mathrm{d}\xi$$

where

$$\mathrm{T} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{V},\xi}$$

and

$$\mathrm{p} = -\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{s},\xi}$$

Symbol ξ represents the chemical composition of the system (and quite generally molecular organization).

The thermodynamic energy of a closed system containing k chemical substances is defined by the independent variables S, V and amounts of each chemical substance.

$$\mathrm{U} = \mathrm{U}\left[\mathrm{S}, \mathrm{V}, \mathrm{n}_1, \mathrm{n}_2 \ldots \mathrm{n}_\mathrm{k}\right]$$

We assert that we can independently add $\delta \mathrm{n}_j$ moles of any one of the k chemical substances in the system and that the entropy S and V can change independently. Based on equation (f), the following (often called the Gibbs equation) is a key relationship.

$$\mathrm{dU} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{V,n(i)}} \mathrm{dS} + \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S,n(i)}} \mathrm{dV} + \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{k}} \left(\frac{\partial \mathrm{U}}{\partial \mathrm{n_j}}\right)_{\mathrm{s,V,n(i\neq j)}} \mathrm{dn_j}$$

Here $\mathrm{n(i)}$ represents the amounts of each of the k chemical substances in the system. Hence from equation (e),

$$\mathrm{dU} = \mathrm{T}\,\mathrm{dS} - \mathrm{p}\,\mathrm{dV} + \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{k}} \left(\frac{\partial \mathrm{U}}{\partial \mathrm{n_j}}\right)_{\mathrm{s,V,n(i\neq j)}} \mathrm{dnj_j}$$

The importance of these equations is indicated by imagining a closed system held at constant volume ($\mathrm{dV} = 0$) and entropy ($\mathrm{dS} = 0$). Under these constraints $\mathrm{dU(S\ and\ V}$ = constant) equals - $\mathrm{A}\ \mathrm{d}\xi$. But according to equation(c), the product $\mathrm{A}\ \mathrm{d}\xi$ is always positive for spontaneous reactions. Hence $\mathrm{dU(S\ and\ V}$ = constant) is negative. In other words, all spontaneous chemical reactions in a closed system at constant S and constant V proceed in a direction which lowers the thermodynamic energy U of the system. This conclusion is universal, independent of the type of chemical reaction and of the mechanism of chemical reaction. For this reason the thermodynamic energy is the thermodynamic potential function for processes in closed systems at constant S and constant V [1].

There is however a problem in terms of practical chemistry. We can envisage designing a reaction vessel which has constant volume. In fact we would probably use heavy steel walls because the conclusions reached above tell us nothing about a possible

change in pressure as we face the challenge of holding the volume constant. But it is not obvious what we have to do to hold the entropy constant. Clearly the line of argument is important. Indeed a similar analysis based on the definitions of enthalpy H, Helmholtz energy F and Gibbs energy G leads to the following three key equations for changes in enthalpy, Helmholtz energy and Gibbs energy respectively.

$$\mathrm{dH} = \mathrm{T\,dS} + \mathrm{V\,dp} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \left(\frac{\partial \mathrm{H}}{\partial \mathrm{n_j}}\right)_{\mathrm{S,p,n(i\neq j)}} dn_j$$

$$\mathrm{dF} = -\mathrm{S\,dT} - \mathrm{p\,dV} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \left(\frac{\partial F}{\partial n_\mathrm{j}}\right)_{\mathrm{T,V,n(i\neq j)}} \mathrm{dn_j}$$

$$\mathrm{dG} = -\mathrm{S\,dT} + \mathrm{V\,dp} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \left(\frac{\partial \mathrm{G}}{\partial n_\mathrm{j}}\right)_{\mathrm{T,p,n(i\neq j)}} \mathrm{dnj_j}$$

The four partial derivatives with respect to n_j in the four equations define the chemical potential, μ_j.

$$\mu_\mathrm{j} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{n_j}}\right)_{\mathrm{s,v,n(}i\neq\mathrm{j)}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{n_j}}\right)_{\mathrm{S,p,n(}i\neq\mathrm{j)}} = \left(\frac{\partial \mathrm{F}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,V,n(i\neq j)}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_j}}\right)_{\mathrm{T,p,n(i\neq j)}}$$

For example,

$$\mathrm{dG} = -\mathrm{S\,dT} + \mathrm{V\,dp} + \sum_{\mathrm{j=1}}^{\mathrm{j=k}} \mu_\mathrm{j}\,\mathrm{dn_j}$$

In context of chemistry, the latter equation is very important.

Footnote

[1] An analogy is drawn with electric potential. In an electrical circuit, electric charge flows spontaneously from high to low electric potential.

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1.14.44: Maxwell Equations

Important relationships[1] in thermodynamics are based on Maxwell Equations [2-4]. Consider the state variable G for a given closed system characterized by the two independent variables, T and p. Hence,

$$\partial^2 \mathrm{G}/\partial \mathrm{T}\,\partial \mathrm{p} = \partial^2 \mathrm{G}/\partial \mathrm{p}\,\partial \mathrm{T}$$

or,

$$\left(\frac{\partial[\partial \mathrm{G}/\partial \mathrm{T}]_{\mathrm{p}}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \left(\frac{\partial[\partial \mathrm{G}/\partial \mathrm{p}]_{\mathrm{T}}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

But at both fixed composition ξ and at equilibrium, $\mathrm{A} = 0$, $\mathrm{V} = [\partial \mathrm{G}/\partial \mathrm{p}]_{\mathrm{T}}$ and $\mathrm{S} = -[\partial \mathrm{G}/\partial \mathrm{T}]_{\mathrm{p}}$

Then

$$\mathrm{E}_{\mathrm{p}} = -(\partial \mathrm{S}/\partial \mathrm{p})_{\mathrm{T}} = (\partial \mathrm{V}/\partial \mathrm{T})_{\mathrm{p}}$$

For the most part we use this relationship in the context of an equilibrium displacement; i.e. at $\mathrm{A} = 0$. Equation (c) shows that at equilibrium the isothermal dependence of entropy on pressure equals, with opposite signs, the isobaric dependence of volume on temperature. E_{p} is the isobaric expansion.

This equation has practical importance. Suppose we require for either practical or theoretical reasons the dependence of the molar entropy of water(ℓ), $\mathrm{S}^*(\mathrm{H_2O};\ell)$ on pressure at a given temperature. This has all the signs of being a difficult project. However the Maxwell Equation (c) shows that the information is obtained by measuring the dependence of molar volume $\mathrm{V}^*(\mathrm{H_2O};\ell)$ on temperature at constant pressure, a simpler approach to the problem. Equation (c) finds several important applications. One application concerns the isothermal dependence of enthalpy on pressure. We start with the equation, $\mathrm{H} = \mathrm{G} - \mathrm{T}\,\mathrm{S}$. We are interested in the dependence of the properties of a given system on pressure at, for example, equilibrium, $\mathrm{A} = 0$ and constant temperature. Then,

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right)_{\mathrm{T}} + \mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{p}}\right)_{\mathrm{T}}$$

But at $\mathrm{A} = 0, \mathrm{V} = (\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T}}$. Using equation (c),

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \mathrm{V} - \mathrm{T}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

We see that the isothermal dependence of enthalpy on pressure is readily obtained knowing the volume of a system and its isobaric dependence on temperature. This is another interesting way in which Maxwell equations often simplify tasks facing chemists when probing the properties of systems. In fact equation (e) is fascinating bearing in mind that we can never know the enthalpy H of a system but we can calculate in a straightforward manner using volumetric properties the isothermal dependence of enthalpy on pressure. In fact the integrated form of equation (e) is also useful. For a system at constant temperature [and at either constant composition ξ or at equilibrium, $\mathrm{A} = 0$],

$$\mathrm{H}(\mathrm{T}, \mathrm{p}_2) - \mathrm{H}(\mathrm{T}, \mathrm{p}_1) = \int_{\mathrm{p}_1}^{\mathrm{p}_2} [\,\mathrm{V} - \mathrm{T}\,(\partial \mathrm{V}/\partial \mathrm{T})_{\mathrm{p}}]\,\mathrm{dp}$$

Another important Maxwell Equation is based on the Helmholtz energy, F, of a closed system.

$$\mathrm{F} = \mathrm{F}[\mathrm{V}, \mathrm{T}, \xi]$$

For a closed system at fixed composition ξ (or at equilibrium when $\mathrm{A} = 0$)

$$\left(\frac{\partial[\partial \mathrm{F}/\partial \mathrm{T}]_{\mathrm{V}}}{\partial \mathrm{p}}\right)_{\mathrm{T}} = \left(\frac{\partial[\partial \mathrm{F}/\partial \mathrm{V}]_{\mathrm{T}}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

But, $\mathrm{S} = -\left(\frac{\partial \mathrm{F}}{\partial \mathrm{T}}\right)_{\mathrm{p}}$ and $\mathrm{p} = -\left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$. Hence,

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

The right-hand-side of equation (i) involves the three practical properties, p, V and T. In summary, the isochoric dependence of pressure on temperature equals the isothermal dependence of entropy on volume.

Two interesting Maxwell Equations develop from the Gibbs energy G. For a system at fixed pressure,

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_T = \frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial T}\right)_\xi$$

But $\mathrm{A} = -\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{\mathrm{T,p}}$, and $S = -\left(\frac{\partial G}{\partial T}\right)_{p,\xi}$, Then,

$$\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{p},\xi} = \left(\frac{\partial \mathrm{S}}{\partial \xi}\right)_{\mathrm{T,p}}$$

This interesting equation concerns the temperature dependence of the affinity for spontaneous reaction at fixed pressure and composition. In fact this dependence equals the isothermal-isobaric entropy of reaction, $(\partial \mathrm{S}/\partial \xi)_{\mathrm{T,p}}$.

Also with respect to the Gibbs energy we explore the properties of a closed system at fixed temperature. Thus,

$$\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial \xi}\right) = \frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial p}\right)$$

But, $\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{\mathrm{T,p}} = -\mathrm{A}$, and $\left(\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} = \mathrm{V}$. Then,

$$-\left(\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right)_{\mathrm{T},\xi} = \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T,p}}$$

In other words at constant composition the isothermal dependence of the affinity for spontaneous change on pressure equals (minus) the volume of reaction, $(\partial \mathrm{V}/\partial \xi)_{\mathrm{T,p}}$.

Maxwell Equations are used in the analysis of parameters describing chemical equilibria. In general terms the limiting enthalpy of reaction, $\Delta_\mathrm{r}\mathrm{H}^\infty$ depends on pressure and the limiting volume of reaction. $\Delta_\mathrm{r}\mathrm{V}^\infty$ depends on temperature. Further the entropy of reaction at temperature T, $\Delta_\mathrm{r}\mathrm{S}^\#$ depends on pressure. These complexities signal more complexities in data analysis. Fortunately two Maxwell Equations assist the analysis. [Here ΔrS# refers to the difference between partial molar entropies of reactants and products in solution reference states at a pressure significantly different from the standard pressure.]

The isothermal dependence of entropy of reaction on pressure is related to the isobaric dependence of limiting volume of reactions on temperature.

$$\left[\frac{\partial \Delta_\mathrm{r}\mathrm{S}^\#}{\partial \mathrm{p}}\right]_\mathrm{T} = -\left[\frac{\partial \Delta_\mathrm{r}\mathrm{V}^\infty}{\partial \mathrm{T}}\right]_\mathrm{p}$$

Further the isothermal pressure dependence of the limiting enthalpy of reaction is related to the limiting volume of reaction and its isobaric temperature dependence. Thus,

$$\left[\frac{\partial \Delta_\mathrm{r}\mathrm{H}^\infty}{\partial \mathrm{p}}\right]_\mathrm{T} = \Delta_\mathrm{r}\mathrm{V}^\infty - \mathrm{T}\left[\frac{\partial \Delta_\mathrm{r}\mathrm{V}^\infty}{\partial \mathrm{T}}\right]_\mathrm{p}$$

The relationships offer a check of derived quantities and the numerical analysis when equilibrium constants are reported as functions of temperature and pressure. The beauty of thermodynamics is appreciated when one realizes that these relationships are precise. Discovery that a set of data and associated analyses do not conform to these equations does not disprove these Maxwell Equations. Rather one must conclude that analysis of the original experimental results is flawed. In fact Maxwell Equations offer an interesting exercise in units of derived and measured parameters. The isentropic expansion $\mathrm{E_S}$ is related to the isochoric dependence of entropy on pressure [5,6]. From $\mathrm{U} = \mathrm{U}[\mathrm{S}, \mathrm{V}]$,

$$\partial^2 U/\partial S\,\partial V = \partial^2 U/\partial V\,\partial S$$

Then,

$$(\partial \mathrm{T}/\partial \mathrm{V})_\mathrm{S} = -(\partial \mathrm{p}/\partial \mathrm{S})_\mathrm{V}$$

We invert the latter equation. Hence,

$$E_S = (\partial V/\partial T)_s = -(\partial S/\partial p)_v$$

Two other Maxwell Equations are worthy of note. From,

$$dH = T\,dS + V\,dp - A\,d\xi$$

At equilibrium and fixed composition,

$$[\partial(\partial H/\partial S)_p/\partial p]_S = (\partial T/dp)_S$$

and

$$[\partial(\partial H/\partial p)_s/\partial T]_p = (\partial V/dS)_p$$

Then,

$$(\partial T/\partial p)_s = (\partial V/\partial S)_p$$

From $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$. Then, $(\partial S/\partial V)_T\,(\partial V/\partial p)_T = -(\partial V/\partial T)_p$ Hence, $(\partial S/\partial V)_T = -(\partial p/\partial V)_T\,(\partial V/\partial T)_p$ Then,

$$(\partial p/\partial T)_V = (\partial S/\partial V)_T$$

Footnotes

[1] The extent of information available from thermodynamic partial derivatives is explored by:

a. R. Gilmore, J. Chem. Phys., 1981,75, 5964; 1982,**77**, 5853.
b. M. Ishara, Bull. Chem. Soc. Jpn., 1986,**59**, 5853.
c. E. Grunwald, J. Am. Chem. Soc., 1984,**106**, 5414.

[2] E. F. Caldin comments on 1010 possible relationships; Chemical Thermodynamics, Oxford, 1958 (page 158).

[3] H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry, van Nostrand 1943.

[4] Extending the observation made by A. B. Pippard [The Elements of Classical Thermodynamics, Cambridge, 1957, p. 46], Maxwell Equations are dimensionally homogeneous in that cross-multiplication yields the following pairs of variables;

i. $p - V$,
ii. $T - S$ and
iii. $A - \xi$.

The product of each pair is energy, with unit 'Joule'.

$$T\,S = [K]\ [JK^{-1}] = [J]$$
$$p\,V = [Nm^{-2}]\ [m^3] = [Nm] = [J]$$
$$A\,\xi = [Jmol^{-1}]\ [mol] = [J]$$

[5] With reference to equation (o),

$$\left[\frac{\partial \Delta_r H^\infty}{\partial p}\right]_T = [m^3\ mol^{-1}] + [K]\left[\frac{m^3\ mol^{-1}}{[K]}\right] = \frac{[m^3\ mol^{-1}]\ [Nm^{-2}]}{[Nm^{-2}]} = \frac{[Jmol^{-1}]}{[Nm^{-2}]}$$

[6] S. D. Hamann, Aust. J. Chem.,1984,**37**,867.

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1.14.45: Moderation

For a closed system, the dependence of chemical composition ξ on temperature T at affinity A and constant pressure is given by equation (a).

$$\left(\frac{\partial \xi}{\partial T}\right)_{\mathrm{p,A}} = -\left[\frac{\mathrm{A} + (\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}}{\mathrm{T}\,(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}}}\right]$$

Similarly for a closed system, the dependence of chemical composition ξ on pressure at fixed temperature is given by equation (b).

$$\left(\frac{\partial \xi}{\partial \mathrm{p}}\right)_{\mathrm{T,A}} = \left[\frac{(\partial \mathrm{V}/\partial \xi)_{\mathrm{T,p}}}{(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}}}\right]$$

These two equations form the basis of 'Laws of Moderation' for closed systems at chemical equilibrium. These equations yield the sign for the two quantities $\left(\frac{\partial \xi}{\partial T}\right)_{p,A=0}$ and $\left(\frac{\partial \zeta}{\partial p}\right)_{T,A=0}$ which describe the change in composition when a system at equilibrium is perturbed to a neighboring equilibrium state.

We recall that by definition ξ is positive for displacement in composition from reactants to products; $\left(\frac{\partial V}{\partial \xi}\right)_{T,A=0}$ is the volume of reaction. If $\left(\frac{\partial V}{\partial \xi}\right)_{T,A=0}$ is positive, $\left(\frac{\partial \xi}{\partial p}\right)_{T,A=0}$ is negative because $\left(\frac{\partial \mathrm{A}}{\partial \xi}\right)_{\mathrm{T,p}} < 0$. According to equation (b), an increase in pressure favors a swing in the equilibrium position towards more reactants [1].

Similarly it follows from equation (a) that an increase in temperature favors a swing in the equilibrium position towards more reactants for an exothermic reaction [2].

Moderation is a striking example of the Second Law of Thermodynamics in action with reference to the direction of spontaneous changes in a **closed** system following changes in either T or p. Here the stress on the word 'closed' reminds us that these laws of moderation do not apply to open system although the point is not always stressed. Therefore controversy often surrounds what is often called Le Chatelier's Principle.

Consider a closed system in which the following chemical equilibrium is established at defined T and p.

$$xX + yY \Leftrightarrow zZ$$

As often argued, if $\delta \mathrm{n_Y}$ moles of chemical substance Y are added to the system, then the equilibrium amount of chemical substance Z increases. In fact such moderation of composition only occurs if $\sum_{j=1}^{j=i} v_j$ is zero for a chemical equilibrium involving i chemical substances. An interesting case concerns the Haber Synthesis.

$$\mathrm{N_2(g)} + 3\mathrm{H_2(g)} \Leftrightarrow 2\mathrm{NH_3(g)}$$

If in the equilibrium system mole fraction $\mathrm{x\,(N_2)} < 0.5$, addition of a small amount of $\mathrm{N_2(g)}$ leads to an increase in the amount of ammonia. However if $\mathrm{x\,(N_2)} > 0.5$ addition of a small amount of $\mathrm{N_2(g)}$ leads to dissociation of ammonia to form more $\mathrm{N_2(g)}$ and $\mathrm{H_2(g)}$ [3].

Footnotes

[1] This conclusion is called a Theorem of Moderation. Co-author MJB was taught that the outcome was "Nature's Law of Cussedness" ($\equiv$ Obstinacy). An exothermic reaction operates to generate heat so the system responds when the temperature is raised in the direction for which the process is endothermic. This line of argument is not good thermodynamics but does make the point.

[2] Another example of Nature's Obstinacy; see [1]. Note the switch in sign on the r.h.s of equations (a) and (b).

[3] I. Prigogine and R. Defay, Chemical Thermodynamics, transl. D. H. Everett, Longmans - Green, London, 1953, page 268.

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1.14.46: Molality and Mole Fraction

Molality

For a solution prepared using n_j moles of solute and w_s kg of solvent , molality

$$m_j = n_j / w_s$$

Molality m_j expressed in 'molkg^{-1}' is independent of temperature and pressure being defined by the masses of solvent and solute. The solvent may comprise a mixture of liquids, the composition of the solvent being described using mole fractions, weight-per-cent or volume-per-cent.

Mole Fraction

For a closed system comprising $\mathrm{n}_1,\ \mathrm{n}_2,\ \mathrm{n}_3 \ldots\ \mathrm{n}_i$ moles of each k chemical substance, the mole fraction of chemical substance j,

$$\mathrm{x_j} = \mathrm{n_j} / \sum_{\mathrm{k}=1}^{\mathrm{k}=\mathrm{i}} \mathrm{n_k}$$

where

$$\sum_{k=1}^{k=1} x_k = 1$$

Mole fraction xj is independent of temperature and pressure (in the absence of chemical reaction between the chemical substances in the system).

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1.14.47: Newton-Laplace Equation

The Newton-Laplace Equation is the starting point for the determination of isentropic compressibilities of solutions [1,2] using the speed of sound u and density ρ; equation (a) [3].

$$\mathrm{u}^2 = (\kappa_\mathrm{s}\,\rho)^{-1}$$

Densities of liquids and speeds of sound at low frequencies can be precisely measured [4,5] .The isentropic condition means that as the sound wave passes through a liquid the pressure and temperature fluctuate within each microscopic volume but the entropy remains constant. The condition ‘at low frequencies‘ is important because at high frequencies (e.g. > 100 MHz) there is a velocity dispersion and absorption of sound as the sound wave couples with molecular processes within the liquid [2,6,7].

Several points emerge from a consideration of equation (a). For example one might ask --- is it just assumed that the correct term is κ_S and not κ_T? The point is that in their examination of the properties of aqueous solutions and aqueous mixtures authors often write something along the following lines -- ‘we used the Newton-Laplace equation to calculate κ_S from measured speeds of sound’. One might then ask-- can one prove equation (a) and is the proof thermodynamic? Rowlinson states that the speed of sound defined by equation (a) is, and we quote, ‘of course a purely thermodynamic quantity’ [1]. This comment raises the issue as to whether or not the defined quantity equals the measured speed of sound.

Intuitively the task of measuring the isothermal property $\mathrm{K_T}\,[= -(\partial \mathrm{V}/\partial \mathrm{p})_\mathrm{T}]$ might seem less problematic than measuring the isentropic property, $\mathrm{K_s}\,[= -(\partial \mathrm{V}/\partial \mathrm{p})_\mathrm{s}]$. $\mathrm{K_T}$ would be obtained by measuring the change in volume following an increase in pressure. However as Tyrer warned [8] in 1914, the isothermal condition is difficult to satisfy and estimated compressions and compressibilities reported up to that time and in the majority of cases were certainly between isentropic and isothermal values. Tyrer did in fact measure κ_T and calculated κ_S using equation (b).

$$\kappa_\mathrm{S} = \kappa_\mathrm{T} - \mathrm{T}\,[\alpha_\mathrm{p}]^2/\sigma$$

Other authors [9,10] have measured κ_T directly by, for example, the volume increase on sudden decompression of a liquid from high to ambient pressure. Nevertheless the conventional approach uses the Newton-Laplace equation. Historically this subject has its origins in the attempts initiated in the 17th Century to measure the speed of sound in air [11].

A sound wave traveling through a fluid produces a series of compressions and rarefactions. Consequently planes of molecules perpendicular to the direction of the sound waves are displaced. The displacement ε depends on both position x and time t. Thus

$$\varepsilon = \varepsilon[\mathrm{x}, \mathrm{t}]$$

The speed of the sound wave u is related to the displacement ε using equation (d), the wave equation.

$$\left(\partial^2\varepsilon/\partial x^2\right) = \left(1/u^2\right)\,\left(\partial^2\varepsilon/\partial t^2\right)$$

A classic analysis [12] in terms of equation (d) and stress-strain relationships for an isotropic phase using Hooke’s Law yields equation (a). At this stage we could consider both the isothermal compressibility κ_T and the isentropic compressibility κ_S. If equation (a) is correct then, either (a) the speed of sound can be calculated knowing κ_S and ρ, or (b) κ_S can be calculated by measuring speed of sound u and density ρ.

Another line of argument states that equation (a) defines the speed of sound in terms of κ_S and density ρ. The question arises -- is the speed of sound calculated using equation (a) equal to the measured speed of sound?

The analysis up to and including equation (d) was familiar to Newton (I. Newton 1642-1727) [13]. Newton using Boyle's Law assumed that the fluid is an ideal gas and that the compressions and rarefactions are isothermal (and in a thermodynamic sense, reversible); Hence

$$\mathrm{u}^2 = \mathrm{p}/\rho$$

Equation (e) was particularly important to Newton because the three quantities in equation (e) can independently determined for (dry) air. Using the density ρ for air at pressure p one can calculate the speed of sound in air. The agreement between observed and calculated speeds was, somewhat disappointingly, only fair but encouraging. The disagreement was an underestimate by 20% as was noted by Newton.

The argument is interesting in the sense of testing if the analysis yields the measured speed of sound. Clearly the equations do not. An important contribution was made by Laplace [14] who assumed that the compressions and rarefactions are perfect and isentropic; i.e. $\mathrm{p\,V^{\gamma}} =$ constant where γ is the ratio of isobaric and isochoric heat capacities. This is the assertion made by Laplace. The overall condition is isentropic for a gas at temperature T. The condition refers to macroscopic properties. Within each microscopic volume both temperature and pressure fluctuate but the entropy remains constant. [The equilibrium and isentropic conditions mean that there is no loss of heat on compression and no gain of heat on rarefaction when the sound wave passes through the system; everything is in phase.] Assuming that γ is independent of p,

$$\mathrm{u^2} = \gamma\,\mathrm{p}/\rho$$

The point is that Laplace knew γ for (dry) air at $273\ \mathrm{K}$ and standard pressure equals 1.4. With this information Laplace obtained good agreement between theory and experiment for the speed of sound in air. In other words Laplace confirmed his assertion that for air (a fluid with low density, $1.29 \times 10^{-3}\ \mathrm{gcm^{-3}}$) compressions and rarefactions are isentropic and not isothermal. Hence the fame of the Newton-Laplace equation which is based on an assertion. Laplace did not prove that the processes are isentropic but having shown agreement between theory and experiment one must conclude that the assertion is correct for air. Equation (a) is the Newton-Laplace Equation. The key point is that the equation emerges from an Equation of State for isentropic compressions of a particular gas, air. Indeed the success achieved by the Newton-Laplace equation in term of predicting the speed of sound in a gas is noteworthy. However we need to comment on the link between κ_{S} measured directly and obtained from measurements of κ_{T}, \alpha_{\mathrm{p}}\) and $\mathrm{C_p}$ using equation (b) [15]. We direct attention to a given closed system containing liquid water. From a practical standpoint, the difference between isothermal and isentropic compressibilities (cf. equation (b)) written here for the pure liquid water, $\frac{\left[\alpha^*_{\mathrm{pl}}(\ell)\right]^2 \mathrm{V}^*_1(\ell)\,\mathrm{T}}{\mathrm{C}^*_{\mathrm{pl}}(\ell)}$. is reasonably accessible. The molar volume $\mathrm{V}^*_1(\ell)$ is obtained from the density $\rho^*_1(\ell); \alpha^*_{p1}(\ell)$ is obtained from the dependence of density on temperature at fixed pressure.

The molar isobaric heat capacity $\mathrm{C}^*_{p1}(\ell)$ is also experimentally accessible. The most frequently cited data set for $\mathrm{V}^*_1(\ell)$ and $\alpha^*_{p1}(\ell)$ was published by Kell and Whalley in 1965 [16]; see also reference [17]. The isothermal compressibility is less accessible . In 1967 Kell summarized [18] the results obtained by Kell and Whalley [16] and quoted that at 25 Celsius, $\alpha^*_{\mathrm{p1}}(\ell) = 257.05 \times 10^{-6}\ \mathrm{K^{-1}}$ and $\kappa^*_{\mathrm{T1}}(\ell)\ = 45.24\mathrm{Mbar^{-1}}$. In 1969 Millero and co-workers[19] directly measured isothermal compressions of water(ℓ) drawing comparisons with the estimates made by Kell and Whalley [16,17]. They reported that for water(ℓ) at 25 Celsius, $\kappa^*_{\mathrm{Tl}}(\ell)\ = (45.94 \pm 0.06)\mathrm{Matm^{-1}}$. Millero *et al.* comment [19] on the excellent agreement.

In 1970, Kell addressed the issue which is of interest here [18]. Equation (b) is the key to the debate because we obtain an estimate of $\kappa^*_{\mathrm{S1}}(\ell)$ from measured $\kappa^*_{21}(\ell), \alpha^*_{\mathrm{pl}}(\ell),\ \mathrm{V}^*_1(\ell)$ and $\mathrm{C}^*_{\mathrm{pl}}(\ell)$; i.e. $\kappa^*_{\mathrm{S}}(\ell;\ \mathrm{density}\ )$. Alternatively we obtain $\kappa^*_{\mathrm{S1}}(\ell)$ using equation (a); i.e. speed of sound and density yielding κ_{S} (acoustic) . The key question is --- are $\kappa^*_{\mathrm{S}}(\ell;\ \mathrm{density}\ )$ and κ_{S} (acoustic) equal? How confident are we that they are equal? There are no assumptions underlying the calculation of $\kappa^*_{\mathrm{S}}(\ell;\ \mathrm{density}\ )$. In the case of κ_{S} (acoustic), the sound wave perturbs the system isentropically; cf. Laplace analysis. Kell comments [20] that speeds of sound can be precisely measured and also a precise estimate of the defined κ_{S} (acoustic) is obtained. Granted the validity of equation (a) one can re-express equation (b) as an equation for $\kappa^*_{\mathrm{T1}}(\ell)$ in terms of measured $\kappa^*_{\mathrm{S1}}(\ell), \alpha^*_{\mathrm{p1}}(\ell),\ \mathrm{V}^*_1(\ell)$ and $\mathrm{C}^*_{\mathrm{p1}}(\ell)$. Examination of various sets of data showed that κ_{S} (acoustic) has less systematic errors than $\kappa^*_{\mathrm{S}}(\ell;\ \mathrm{density}\ )$ but that they are effectively the same, a point confirmed by Fine and Millero [21].

Footnotes

[1] J. S. Rowlinson and F. L. Swinton, Liquid and Liquid Mixtures, Butterworths, London , 3rd. edn., 1982, pp. 16-17.

[2] J. O. Hirschfelder, C. F. Curtis and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, corrected printing 1964, chapters 5 and 11.

[3]

$$\mathrm{u^2} = \frac{1}{\kappa_{\mathrm{s}}}\,\frac{1}{\rho} = \left[\mathrm{Nm^{-2}}\right]\ \frac{1}{\left[\ \mathrm{kg\ m^{-3}}\right]} = \frac{\left[\mathrm{kgms^{-2}\ m^{-2}}\right]}{\left[\mathrm{kgm^{-3}}\right]} = \left[\mathrm{m^2\ s^{-2}}\right]$$

$$\mathrm{u} = \left[\mathrm{ms^{-1}}\right]$$

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[7] M. J. Blandamer, Introduction to Chemical Ultrasonics, Academic Press,1973.

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[10] L. A. K. Staveley, W. I. Tupman and K. Hart, Trans. Faraday, Soc.,1955,**51**,323.

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[12] S. G. Starling and A. J. Woodhall, Physics, Longmans, London, 2nd edn.,1957.

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[14] S. Laplace, Ann. Chim. Phvs., 1816,**3**,328.

[15] D.-P. Wang and F. J. Millero, J. Geophys. Res.,1973,**78**,7122.

[16] G. S. Kell and E. Whalley, Philos. Trans. R. Soc. London, Ser.A.,1965,**258**,565.

[17] G. S. Kell, G. E. McLaurin and E. Whalley, Proc. R. Soc. London, Ser,.A, 1978, **360**, 389.

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[19] F. J. Millero, R.W. Curry and W. Drost-Hansen, J. Chem. Eng. Data,1969,**14**,422.

[20] G. S. Kell, in Water A Comprehensive Treatise, ed. F. Franks, Plenum Press, New York,1973,volume I, chapter 10.

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1.14.48: Open System

The chemical thermodynamics of open systems [1-2] is more complicated than that of closed systems because chemical substances exchange between system and surroundings, crossing the boundary of the system.

Footnote

[1] D. Kondepudi and I. Prigogine, Modern Thermodynamics; From Heat Engines to Dissipative Structures, Wiley, New York, 1998.

[2] Clearly a treatment of the chemical thermodynamics of the human body has to take account of the fact that such systems are open. Farmers are very practical chemical thermodynamic experts because in feeding their livestock they judge if the animals they are feeding will

i. produce milk for sale,
ii. meat for food,
iii. skin for the manufacture of leather and/or
iv. be used for breeding.

Farmers do not leave these options to chance as they cope in very practical way with such open systems.

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1.14.49: Osmotic Coefficient

There is possible disadvantage in an approach using the mole fraction scale to express the composition of a solution. Granted

i. that our interest is often in the properties of solutes in aqueous solutions,
ii. that the amount of solvent greatly exceeds the amount of solute in a solution, and
iii. that the sensitivity of equipment developed by chemists is sufficient to probe the properties of quite dilute solutions,

the mole fraction scale for the solvent is not the most convenient method for expressing the composition of a given solution [1-3]. Hence another equation relating $\mu_1(\mathrm{aq;T;p})$ to the composition of a solution finds favor.

By definition, for a solution containing a single solute, chemical substance j [4],

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^*(\ell;\mathrm{T;p}) - \phi\,\mathrm{R\,T\,M_1\,m_j}$$

Or, in terms of the standard chemical potential for water at temperature T and standard pressure $\mathrm{p^0}$,

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^*\left(\ell;\mathrm{T;p^0}\right) - \phi\,\mathrm{R\,T\,M_1\,m_j} + \int_{\mathrm{p^0}}^{\mathrm{p}} \mathrm{V_1^*}(\ell;\mathrm{T})\,\mathrm{dp}$$

$\mathrm{M_1}$ is the molar mass of water; ϕ is the practical osmotic coefficient which is characteristic of the solute, molality mj, temperature and pressure. By definition ϕ is unity for ideal solutions at all temperatures and pressures.

$$\mathrm{limit}\,(\mathrm{m_j} \to 0)\,\phi = 1.0 \text{ at all T and p}$$

Further for ideal solutions, the partial differentials $(\partial\phi/\partial T)_p, \left(\partial^2\phi/\partial T^2\right)_p$ and $(\partial\phi/\partial \mathrm{p})_\mathrm{T}$ are zero. For an ideal solution [5],

$$\mu_1(\mathrm{aq;T;p;id}) = \mu_1^*(\ell;\mathrm{T;p}) - \mathrm{R\,T\,M_1\,m_j}$$

We rewrite equation (d) in the following form:

$$\mu_1(\mathrm{aq;T;p;id}) - \mu_1^*(\ell;\mathrm{T;p}) = -\mathrm{R\,T\,M_1\,m_j}$$

Hence with an increase in molality of solute in an ideal aqueous solution, the solvent is stabilized, being at a lower chemical potential than that for pure water. We contrast the chemical potentials of the solvent in real and ideal solutions using an excess chemical potential, $\mu_1^E(aq;T;p)$;

$$\begin{aligned}\mu_1^{\mathrm{E}}(\mathrm{aq;T;p}) &= \mu_1(\mathrm{aq;T;p}) - \mu_1(\mathrm{aq;id;T;p}) \\ &= (1-\phi)\,\mathrm{R\,T\,M_1\,m_j}\end{aligned}$$

The term $(1-\phi)$ is often encountered because it expresses succinctly the impact of the solute on the properties of the solvent. At a given molality (and fixed temperature and pressure), ϕ is characteristic of the solute.

In the case of a salt j which on complete dissociation forms ν ions the analogue of equation (a) takes the following form.

$$\mu_1(\mathrm{aq;T;p}) = \mu_1^*(\ell;\mathrm{T;p}) - \mathrm{v}\,\phi\,\mathrm{R\,T\,M_1\,m_j}$$

Footnotes

[1] N. Bjerrum, Z. Electrochem., 1907, **24**,259.

[2] G. N. Lewis and M. Randall, Thermodynamics, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 2nd edn., 1961, chapter 22.

[3] Mole fractions of solvent x_1 for aqueous solutions having gradually increasing molality of solute \(\mathrm{m}_{j}.

(A)	$m_j/molkg^{-1} = 10^{-3}$;	$x_1 = 0.999982$	$x_j = 1.8 \times 10^{-5}$
(B)	$m_j/molkg = 10^{-2}$;	$x_1 = 0.99982$	$x_j = 1.8 \times 10^{-4}$
(C)	$m_j/molkg = 10^{-1}$;	$x_1 = 0.9982$	$x_j = 1.8 \times 10^{-3}$
(D)	$m_j/molkg^{-1} = 0.5$;	$x_1 = 0.9911$	$x_j = 8.9 \times 10^{-3}$
(E)	$m_j/molkg = 1.0$	$x_1 = 0.9823$	$x_j = 1.77 \times 10^{-2}$

[4]

$$[\mathrm{Jmol^{-1}}] = [\mathrm{Jmol^{-1}}] - [1]\ [\mathrm{JK^{-1}\ mol^{-1}}]\ [\mathrm{K}]\ [\mathrm{kgmol^{-1}}]\ [\mathrm{molkg^{-1}}]$$

The definitions of ideal solutions expressed in equations (i) and (ii) are not in conflict.

$$\mu_1(\mathrm{aq;T;p;id}) = \mu_1^*(\ell;\mathrm{T;p}) - \mathrm{R\,T\,M_1\,m_j}$$

$$\mu_1(\mathrm{aq;T;p;id}) = \mu_1^*(\ell;\mathrm{T;p}) + \mathrm{R\,T\,\ln(x_1)}$$

Thus for an ideal solution these equations require that, $v - \mathrm{M_1\,m_j} = \ln(\mathrm{x_1})$ But

$$\ln(\mathrm{x_1}) = \ln\left[\mathrm{M_1^{-1}}/\left(\mathrm{M_1^{-1}} + \mathrm{m_j}\right)\right] = -\ln(1.0 + \mathrm{m_j\,M_1})$$

Bearing in mind that $\mathrm{M_1} = 0.018\ \mathrm{kgmol^{-1}}$, then for dilute solutions $\ln(1.0 + \mathrm{m_j\,M_1}) = \mathrm{m_j\,M_1}$.

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1.14.50: Osmotic Pressure

A semi-permeable membrane [1] separates an aqueous solution (where the mole fraction of water equals x_1) and pure solvent at temperature T and ambient pressure. Solvent water flows spontaneously across the membrane thereby diluting the solution. This flow is a consequence of the chemical potential of the solvent in the solution being lower than the chemical potential of pure solvent at the same T and p. If a pressure $(p + \pi)$ is applied to the solution, the spontaneous process stops because the solution at pressure $(p + \pi)$ and the solvent at pressure p are in thermodynamic equilibrium; π is the osmotic pressure. Thus at equilibrium,

$$\mu_1(aq; T; p + \pi) = \mu_1^*(\ell; T; p)$$

Under this equilibrium condition solvent flows in both directions across the semi-permeable membrane but the net flow is zero. In the analysis presented here we take account of the fact, writing p' for $(p + \pi)$, the chemical potential of water in the aqueous solution is given by equation (b).

$$\mu_1^{eq}(aq; T; p') = \mu_1^*(\ell; T; p = 0) + p'\, V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, K_{T1}^*(\ell)\, p'] + R\, T\, \ln(x_1\, f_1)$$

Here f_1 is the activity coefficient expressing the extent to which the thermodynamic properties of water in the aqueous solution are not ideal. For the pure solvent water at pressure p (i.e. on the other side the of the semi-permeable membrane),

$$\mu_1^{eq}(aq; T; p) = \mu_1^*(\ell; T; p = 0) + p'\, V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, \kappa_{T1}^*(\ell)\, p]$$

But osmosis experiments explore an equilibrium characterized by equation (d).

$$\mu_1(aq; T; p') = \mu_1^*(\ell; T; p)$$

Therefore using equations (b) and (c),

$$p'\, V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, \kappa_{T1}^*(\ell)\, p'] + R\, T\, \ln(x_1\, f_1) = p\, V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, \kappa_{T1}^*(\ell)\, p]$$

Or,

$$p\, V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, \kappa_{T1}^*(\ell)\, p'] - p\, V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, \kappa_{T1}^*(\ell)\, p] = -R\, T\, \ln(x_1\, f_1)$$

The terms $V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, \kappa_{T1}^*(\ell)\, p']$ and $V_1^*(\ell; T; p = 0)\, [1 - (1/2)\, \kappa_{T1}^*(\ell)\, p]$ describe the molar volumes of water at pressures p and p'; i.e. at pressure p and $(p + \pi)$. We assume that both terms can be replaced by the molar volumes at average pressure $[(2\, p + \pi)/2]$; namely $V_1^*[\ell; T; (2\, p + \pi)/2]$. Therefore

$$\pi\, V_1^*(\ell; T; (2\, p + \pi)/2] = -R\, T\, \ln(x_1\, f_1)$$

In the event that $\pi << 2\, p$,

$$\pi\, V_1^*[\ell; T; p] = -R\, T\, \ln(x_1\, f_1)$$

If the thermodynamic properties of the solutions are ideal, f_1 equals unity. Then

$$\pi^{id}\, V_1^*[\ell; T; p] = -R\, T\, \ln(x_1)$$

In the latter two equations $V_1^*(\ell; T; p)$ is treated as a constant, independent of the thermodynamic properties of the solution. A further interesting development of equation (i) is possible for a solution prepared using n_1 moles of solvent water and n_j moles of solute. Thus

$$-\ln(x_1) = \ln\left(\frac{1}{x_1}\right) = \ln\left(\frac{n_1 + n_j}{n_1}\right) = \ln\left(1 + \frac{n_j}{n_1}\right)$$

But . $(n_j/n_1) << 1$. We expand the last term in equation (j).

$$\ln\left(1+\frac{n_j}{n_1}\right)=\frac{n_j}{n_1}-\frac{1}{2}\left(\frac{n_j}{n_1}\right)^2+\frac{1}{3}\left(\frac{n_j}{n_1}\right)^3-\ldots..$$

If we retain only the first term;

$$\pi^{id}\,V_1^*[\ell;T;p]=R\,T\;(n_j/n_1)$$

But for a dilute solution, the volume of the solution V is given by $\mathbf{n}_1\,V_1^*[\ell;T;p]$.

Or [2],

$$\pi^{id}\,V(aq)=n_j\,R\,T$$

But concentration

$$c_j=n_j/V$$

Then [3]

$$\pi^{id}=c_j\,R\,T$$

Agreement between $\pi(obs)$ and π^{id} for aqueous solutions containing neutral solutes (e.g. sucrose) confirms the validity of the thermodynamic analysis.

Footnotes

[1] The term 'semi-permeable' in the present context means that the membrane is only permeable to the solvent. Perhaps the optimum semipermeable membrane is the vapor phase.

[2] Historically, equation(o) owes much to the equation of state for an ideal gas; i.e. $p\,V=n\,R\,T$. From an experimentally found proportionality between π and c_j, van't Hoff showed that the proportionality constant can be approximated by $R\,T$.

[3]

$$\pi=[molm^{-3}]\;[JK^{-1}\,mol^{-1}]\;[K]=[Jm^{-3}]=[Nmm^{-3}]=[Nm^{-2}]$$

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1.14.51: Partial Molar Properties: General

The laws of thermodynamics and the associated treatment of the thermodynamic properties of closed systems concentrate attention on macroscopic properties. Although we may define the composition of a closed system in terms of the amounts of each chemical substance in a system, general thermodynamic treatments direct our attention to macroscopic properties such as, volume V, Gibbs energy G, enthalpy H and entropy S. We need to 'tell' these thermodynamic properties that a given system probably comprises different chemical substances. In this development the analysis is reasonably straightforward if we define the system under consideration by the 'Gibbsian 'set of independent variables; i.e. $\mathrm{T},\ \mathrm{p}$ and amounts of each chemical substance. Thus,

$$\mathrm{G} = \mathrm{G}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2, \ldots \mathrm{n}_\mathrm{i}\right]$$

In equation (a), the Gibbs energy is defined by intensive variables T and p together with extensive composition variables. In many cases the task of a chemist is to assay a system to determine the number and amounts of each chemical substance in the system.

The analysis leads to the definition of the chemical potential for each substance j, μ_j in a closed system.

Consider a solution comprising n_1 moles of solvent, liquid chemical substance 1, and n_j moles of solute, chemical substance j. We ask—what contributions are made by the solvent and by the solute to the volume of the solution at defined T and p? In fact we can only guess at these contributions [1]. This is disappointing. The best we can do is to probe the sensitivity of the volume of a given solution to the addition of small amounts of either solute or solvent. This approach leads to a set of properties called partial molar volumes. Here we explore the definition of these properties. The starting point is the Gibbs energy of a solution. We develop the argument in a way which places the Gibbs energy at the centre from which all other thermodynamic variables develop. For a closed system containing i-chemical substances,

$$\mathrm{G} = \sum_{\mathrm{j}=1}^{\mathrm{j}=\mathrm{i}} \mathrm{n}_\mathrm{j}\, \mu_\mathrm{j}$$

The later equation signals that the total Gibbs energy is given by the sum of products of amounts and chemical potentials of each chemical substance in the system. For an aqueous solution containing n_j moles of solute j and n_1 moles of solvent 1 (water),

$$G(aq) = n_1\, \mu_1(aq) + n_j\, \mu_j(aq)$$

We do not have to attach to equation (c) the condition 'at fixed $\mathrm{T} and \mathrm{p}$'. Similarly the volume of the solution is given by equation (d).

$$V(aq) = n_1\, V_1(aq) + n_j\, V_j(aq)$$

The same argument applies in the case of a system prepared using n_1 moles of water, n_X moles of solute X and n_Y moles of solute Y.

$$\mathrm{G(aq)} = \mathrm{n}_1\, \mu_1(\mathrm{aq}) + \mathrm{n}_\mathrm{X}\, \mu_\mathrm{X}(\mathrm{aq}) + \mathrm{n}_\mathrm{Y}\, \mu_\mathrm{Y}(\mathrm{aq})$$

Complications emerge however if solute X and Y are in chemical equilibrium; e.g. $X(aq) \Leftrightarrow Y(aq)$. Then account must be taken of the fact that $\mathrm{n}_\mathrm{x}^{\mathrm{eq}}$ and $\mathrm{n}_\mathrm{x}^{\mathrm{eq}}$ depend on T and p.

Footnote

[1] I have on my desk a flask containing water ($\ell; 100\ \mathrm{cm}^3$) and 20 small round steel balls, each having a volume of $0.1\ \mathrm{cm}^3$. I add a steel ball to the flask and the volume of the system, water + steel ball, is $100.1\ \mathrm{cm}^3$. I add one more steel ball and the volume of the system increases by $0.1\ \mathrm{cm}^3$. So in this simple case I can equate directly the volume of the pure steel balls V^*(balls) with the partial molar volume of the balls in the system, water + balls.

I have on my desk an empty egg carton designed to hold six eggs. The volume of the carton is represented as $\mathrm{V(c)}$ as judged by the volume occupied in a food store.. The volume of one egg is V^*(egg), the superscript * indicating that we are discussing the property of pure eggs. I now 'add' one egg to the egg carton which does not change its volume ----again as judged by the volume occupied in a food store. In other words the partial molar volume of eggs in the egg carton $\mathrm{V(egg)}$ is zero;

$$V(\text{ egg }) = \left(\frac{\partial V(\text{ system })}{\partial n(\text{ egg })}\right) = \text{ zero. Or, } V(\text{ egg }) - V^*(\text{ egg }) < 0$$

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1.14.52: Partial Molar Properties: Definitions

A given liquid mixture is prepared using $\mathrm{n_1}$ moles of liquid 1 and $\mathrm{n_2}$ moles of liquid 2. If the thermodynamic properties of the liquid mixture are ideal the volume of the mixture is given by the sum of products of amounts and molar volumes (at the same T and p); equation (a).

$$\mathrm{V(mix;id)} = \mathrm{n_1\,V_1^*}(\ell) + \mathrm{n_2\,V_2^*}(\ell)$$

If the thermodynamic properties of the mixture are not ideal, the volume of the (real) mixture is given by equation (b).

$$\mathrm{V(mix)} = \mathrm{n_1\,V_1(mix)} + \mathrm{n_2\,V_2(mix)}$$

$\mathrm{V_1(mix)}$ and $\mathrm{V_1(mix)}$ are the partial molar volumes of chemical substances 1 and 2 defined by equations (c) and (d).

$$V_1(mix) = \left(\frac{\partial V}{\partial n_1}\right)_{T,p,n(2)}$$

$$V_2(\mathrm{mix}) = \left(\frac{\partial V}{\partial n_2}\right)_{T,p,n(1)}$$

The similarities between equations (a) and (b) are obvious and indicate an important method for describing the extensive properties of a given system. This was the aim of G. N. Lewis [1] who sought equations of the form shown in equation (b). In general terms, we identify an extensive property X of a given system such that the variable can be written in the general form shown in equation (e).

$$\mathrm{X} = \mathrm{n_1\,X_1} + \mathrm{n_2\,X_2}$$

where

$$\mathrm{X_1} = \left(\frac{\partial \mathrm{X}}{\partial \mathrm{n_1}}\right)_{\mathrm{T,p,n(2)}}$$

$$X_2(\mathrm{mix}) = \left(\frac{\partial X}{\partial n_2}\right)_{T,p,n(1)}$$

Other than the composition variables, the conditions on the partial differentials in equations (f) and (g) are intensive properties;

i. mechanical variable, pressure, and
ii. thermal variable, temperature.

Partial molar properties can also be defined for different pairs of intensive thermal and non-thermal variables, other than T and p [2]. The concept of a partial property was extended to intensive properties such as isothermal and isentropic compressibilities [3].

A further distinction between Lewisian and non-Lewisian partial molar properties has been proposed [2,4].

Footnotes

[1] G. N. Lewis, Proc. Am. Acad. Arts Sci.,1907,**43**,259.

[2] J. C. R. Reis, J. Chem. Soc Faraday Trans.,2,1982,**78**,1575.

[3] J. C. R. Reis, J. Chem. Soc Faraday Trans.,1998,**94**,2385.

[4] J. C. R. Reis, M. J. Blandamer, M. I. Davis and G. Douheret, Phys. Chem.Chem.Phys.,2001,**3**,1465.

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1.14.53: Phase Rule

According to the Gibbs-Duhem Equation, the properties of a single phase at equilibrium containing i chemical substances are related; we divide the Gibbs-Duhem Equation by the total amount in the system such that $\mathrm{x}_j(\alpha)$ is the mole fraction of substance j in the α phase. The Gibbs-Duhem Equation. requires that

$$0 = \mathrm{S_m}(\alpha)\,\mathrm{dT} - \mathrm{V_m}(\alpha)\,\mathrm{dp} + \sum_{\mathrm{j=1}}^{\mathrm{j=i}} \mathrm{x_j}(\alpha)\,\mathrm{d}\mu_\mathrm{j}(\alpha)$$

Within this phase, the definition of mole fraction means that over all i-chemical substances,

$$\sum_{j=1}^{j=i} x_j(\alpha) = 1$$

The number of independent intensive variables is $[\mathrm{P}\ (\mathrm{C}-1)+2]$ where C is the number of independent chemical substances in phase α. The additional two variables refer to the intensive temperature and pressure. We consider the case where the closed system contains P phases. Therefore we can set down P equations of the form shown in equation (a). With reference to the chemical potential of substance j, the overall equilibrium condition requires that the chemical potentials of this substance over all phases (i.e. $\alpha_1, \alpha_2, \alpha_3, \ldots\ldots\alpha_p$) are equal.

$$\mu_j(\alpha_1) = \mu_j(\alpha_2) = \mu_j(\alpha_3) = \ldots\ldots\ldots\ldots = \mu_j(\alpha_p)$$

Hence with reference to the intensive chemical potentials there are $(\mathrm{P}-1)$ constraints. Therefore the number of independent intensive variables for this system comprising i chemical substances distributed through P phases, namely F, equals $(\mathrm{C}-1)+2-(\mathrm{P}-1)$. Therefore

$$\mathrm{P} + \mathrm{F} = \mathrm{C} + 2$$

The latter is the Phase Rule. This equation is possibly the most elegant and practical equation in chemistry.

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1.14.54: Poynting Relation

A given closed system comprises chemical substance j in two homogeneous subsystems which are separated by an appropriate semipermeable diaphragm and which are at the same temperature but different pressures. The subsystems I and II are in thermodynamic equilibrium. Thus (cf. Topic 690),

$$\mu_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1) = \mu_j^* (\mathrm{II}, \mathrm{T}, \mathrm{p}_2)$$

For subsystem I,

$$\mathrm{d}\mu_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1) = \left(\frac{\partial \mu_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)}{\partial \mathrm{T}} \right)_{\mathrm{p}} \mathrm{dT} + \left(\frac{\partial \mu_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)}{\partial \mathrm{p}} \right)_{\mathrm{T}} \mathrm{dp}_1$$

Or,

$$\mathrm{d}\mu_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1) = -\mathrm{S}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)\ \mathrm{dT} + \mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)\ \mathrm{dp}_1$$

Here $\mathrm{S}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)$ and $\mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_\mathrm{l})$ are molar properties of chemical substance j. Similarly,

$$\mathrm{d}\mu_j^* (\mathrm{II}, \mathrm{T}, \mathrm{p}_2) = -\mathrm{S}_j^* (\mathrm{II}, \mathrm{T}, \mathrm{p}_2)\ \mathrm{dT} + \mathrm{V}_j^* (\mathrm{II}, \mathrm{T}, \mathrm{p}_2)\ \mathrm{dp}_2$$

The equality expressed in equation (a) is valid at all T and p. Clearly this condition can only be satisfied if the following equation is satisfied.

$$\mathrm{d}\mu_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1) = \mathrm{d}\mu_j^* (\mathrm{II}, \mathrm{T}, \mathrm{p}_2)$$

Then at constant temperature,

$$V_j^* (I, T, p_1)\ dp_1 = V_j^* (II, T, p_2)\ d_2$$

Hence,

$$\frac{\mathrm{dp}_1}{\mathrm{dp}_2} = \frac{\mathrm{V}_j^* (\mathrm{II}, \mathrm{T}_1, \mathrm{p}_2)}{\mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)}$$

The latter is the Poynting Equation [1]. An interesting application of this equation concerns the case where system II is the vapor phase and system I is the liquid phase. The vapor phase is described as an ideal gas using equation (h) for one mole of chemical substance j.

$$\mathrm{p}_2\, \mathrm{V}_j^* (\mathrm{II}, \mathrm{T}, \mathrm{p}_2) = \mathrm{R}\, \mathrm{T}$$

The liquid phase comprises one mole of liquid j for which $\mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)$ is the molar volume which is assumed to be a constant, independent of pressure.

Hence from equations (g) and (h),

$$\frac{\mathrm{dp}_1}{\mathrm{dp}_2} = \frac{1}{\mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)} \frac{\mathrm{R}\, \mathrm{T}}{\mathrm{p}_2}$$

Or,

$$\mathrm{R}\, \mathrm{T}\, \mathrm{d} \ln (\mathrm{p}_2) = \mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)\ d\mathrm{p}_1$$

The assumption is made that, phase I being a liquid, $\mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)$ is independent of pressure. Then equation (j) is integrated between pressure limits p_2 and $\mathrm{p}_2{}'$ and between p_1 and $\mathrm{p}_1{}'$. Hence,

$$\mathrm{R}\, \mathrm{T}\ \ln (\mathrm{p}_2'/\mathrm{p}_2) = \mathrm{V}_j^* (\mathrm{I}, \mathrm{T}, \mathrm{p}_1)\ [\mathrm{p}_1' - \mathrm{p}_1]$$

An interesting application of equation (k) concerns the impact of an increase in pressure from p_1 and $\mathrm{p}_1{}'$ on liquid j. This increase might be produced for example by an increase in confining pressure of an inert gas insoluble in liquid j. Equation (k) describes the increase in vapor pressure from p_2 to $\mathrm{p}_2{}'$ of liquid j. This pattern might seem intuitively somewhat unexpected.

Footnotes

[1] J. J. Vanderslice, H. W. Schamp Jr and E. A. Mason, Thermodynamics, Prentice Hall,Englewood Cliffs, N.J., 1966, page 106.

[2] Poynting, Phil. Mag.,1881,[4],**12**,32.

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1.14.55: Process

In order to document the thermodynamics of processes a convention has been agreed. In general, the thermodynamic variable takes the following form.

$$\Delta_{\mathrm{proc}}\,\mathrm{X}^{0}$$

Here

i. Δ signals a change is the thermodynamic extensive variable X;
ii. the subscript 'proc' signals the process; e.g.

- $\mathrm{f} =$ formation
- $\mathrm{c} =$ combustion
- $\mathrm{vap} =$ vaporisation
- $\mathrm{r} =$ chemical reaction
- $\mathrm{aln} =$ = solution

In recognition of the long tradition of using a 'double-dagger', a superscript $\neq$ indicates activation as in the formation of 'transition state from reactants.

ii. the superscript '0' means under standard conditions which should be defined. Example.

- $\Delta_{\mathrm{c}}\mathrm{H}^{0} =$ standard enthalpy of combustion
- $\Delta^{\neq}\mathrm{V}^{0} =$ standard volume of activation

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1.14.56: Properties: Equilibrium and Frozen

A given closed system having Gibbs energy G at temperature T, pressure p, molecular composition (organization ξ) and affinity for spontaneous change A is described by equation (a).

$$\mathrm{G} = \mathrm{G}[\mathrm{T}, \mathrm{p}, \xi]$$

In the state defined by equation (a), there is an affinity for spontaneous chemical reaction A. Starting with the system in the state defined by equation (a) it is possible to change the pressure and perturb the system to a series of neighboring states for which affinity remains constant. The differential dependence of G on pressure for the original state along the path at constant A is given by $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T,A}}$. Returning to the original state characterized by T, p and ξ, we imagine that it is possible to perturb the system by a change in pressure in such a way that the system remains at fixed extent of reaction, ξ. The differential dependence of G on pressure for the original state along the path at constant ξ is given by $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T},\xi}$. We explore these dependences of G on pressure at fixed temperature and at

i. fixed composition, ξ and
ii. fixed affinity for spontaneous change, A.

The procedure for relating $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T,A}}$, and $(\partial \mathrm{G}/\partial \mathrm{p})_{\mathrm{T},\xi}$ is a standard calculus operation. At fixed temperature,

$$\left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\mathrm{A}} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\xi} - \left[\frac{\partial \mathrm{A}}{\partial \mathrm{p}}\right]_{\xi} \left[\frac{\partial \xi}{\partial \mathrm{A}}\right]_{\mathrm{p}} \left[\frac{\partial \mathrm{G}}{\partial \xi}\right]_{\mathrm{p}}$$

This interesting equation shows that the differential dependence of Gibbs energy (at constant temperature) on pressure at constant affinity for spontaneous change does NOT equal the corresponding dependence at constant extent of chemical reaction. This inequality is not surprising. But our interest is drawn to the case where the system under discussion is, at fixed temperature and pressure, at thermodynamic equilibrium where A is zero, $\mathrm{d}\xi/\mathrm{dt}$ is zero, Gibbs energy is a minimum AND, significantly, $(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}}$ is zero. Hence

$$\mathrm{V} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\mathrm{T,A}=0} = \left[\frac{\partial \mathrm{G}}{\partial \mathrm{p}}\right]_{\mathrm{T},\xi^{\mathrm{eq}}}$$

The dependence of G on pressure for differential displacements at constant '$\mathrm{A} = 0$' and ξ^{eq} are identical. We confirm that the volume V of a system is a 'strong' state variable. These comments seem trivial but the point is made if we go on to consider the volume of a system as a function of temperature at constant pressure. We use a calculus operation to derive equation (d).

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{A}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\xi} - \left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\xi} \left(\frac{\partial \xi}{\partial \mathrm{A}}\right)_{\mathrm{T}} \left(\frac{\partial \mathrm{V}}{\partial \xi}\right)_{\mathrm{T}}$$

Again we are not surprised to discover that in general terms the differential dependence of V on temperature at constant affinity does not equal the differential dependence of V on temperature at constant composition/organization. Indeed, unlike the simplification we could use in connection with equation (b), {namely that at equilibrium $(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}}$ is zero} we cannot assume that the volume of reaction, $(\partial \mathrm{V}/\partial \xi)_{\mathrm{T,p}}$ is zero at equilibrium. In other words for a closed system at thermodynamic equilibrium at fixed T and fixed p {when $\mathrm{A} = 0$, $\xi = \xi^{\mathrm{eq}}$ and $\mathrm{d}\xi^{\mathrm{eq}}/\mathrm{dt} = 0$}, there are two thermal expansions, at constant A and at constant ξξ.

We consider a closed system in equilibrium state I defined by the set of variables, $\{\mathrm{T[I]}, \mathrm{p}, \mathrm{A} = 0, \xi^{\mathrm{eq}}[\mathrm{I}]\}$. The equilibrium composition is $\xi^{\mathrm{eq}}[\mathrm{I}]$ at zero affinity for spontaneous change. This system is perturbed to two nearby states at constant pressure.

a. State I is displaced to a nearby equilibrium state II defined by the set of variables, $\{\mathrm{T[I]} + \delta\mathrm{T}, \mathrm{p}, \mathrm{A} = 0, \xi^{\mathrm{eq}}[\mathrm{II}]\}$. This equilibrium displacement is characterized by a volume change;

$$\Delta \mathrm{V}(\mathrm{A} = 0) = \mathrm{V[II]} - \mathrm{V[I]}$$

$$\mathrm{E_p}(\mathrm{A} = 0) = \left[\frac{\mathrm{V[II]} - \mathrm{V[I]}}{\Delta \mathrm{T}}\right]_{\mathrm{p,A}=0}$$

The equilibrium isobaric expansibility,

$$\alpha_{\mathrm{p}}(\mathrm{A} = 0) = \mathrm{E_p}(\mathrm{A} = 0)/\mathrm{V}$$

In order for the system to move from one equilibrium state, I with composition $\xi^{eq}[I]$ to another equilibrium state, II with composition $\xi^{eq}[II]$, the system changes by a change in chemical composition and/or molecular organization.

b.

Hence we define the 'frozen' isobaric expansion, $E_p(\xi = \text{fixed})$. An alternative name is the instantaneous expansion because, practically, we would have to change the temperature at a such a high rate that there is no change in molecular composition or organisation in the system.

$$E_p(\xi = \text{ fixed }) = \left(\frac{\partial V}{\partial T}\right)_{p,\xi}$$

Further

$$\alpha_p(\xi = \text{ fixed }) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\xi}$$

Similar comments apply to isothermal compressibilities, K_T; there are two limiting quantities $\kappa_T(A = 0)$ and $\kappa_T(\xi)$. In order to measure $\kappa_T(\xi)$ we have to change the pressure also in an infinitely short time.

The entropy S is given by the partial differential, $-(\partial G/\partial T)_{p,\xi}$. At equilibrium where $A = 0,\ S = -(\partial G/\partial T)_{p,A=0}$. We carry over the argument described in the previous section but now concerned with a change in temperature. We consider the two pathways, constant A and constant ξ.

$$(\partial G/\partial T)_{p,A} = (\partial G/\partial T)_{p,\xi} - (\partial \xi/\partial A)_{T,p}\,(\partial A/\partial T)_{p,\bar{\xi}}\,(\partial G/\partial \xi)_{T,p}$$

But at equilibrium, A which equals $-(\partial G/\partial \xi)_{T,p}$ is zero, and so $S(A = 0)$ equals $S\,(\xi^{eq})$. Then just as for volumes, the entropy of a system is not a property concerned with pathways between states; entropy is a strong function of state. Another important link involving Gibbs energy and temperature is provided by the Gibbs-Helmholtz equation. We explore the relationship between changes in (G/T) at constant affinity A and at fixed ξ, following perturbation by a change in temperature.

$$[\partial(G/T)/\partial T]_{p,A} = [\partial(G/T)/\partial T]_{p,\xi} - (1/T)\,(\partial \xi/\partial A)_{T,p}\,(\partial A/\partial T)_{p,\xi}\,(\partial G/\partial \xi)_{T,p}$$

But at equilibrium, A which equals $-(\partial G/\partial \xi)_{T,p}$ is zero. Then $H(A = 0) = H\,(\xi^{eq})$. In other words, the variable enthalpy is another strong function of state. This is not the case for isobaric heat capacities.

$$(\partial H/\partial T)_{p,A} = (\partial H/\partial T)_{p,\xi} - (\partial \xi/\partial A)_{T,p}\,(\partial A/\partial T)_{p,\xi}\,(\partial H/\partial \xi)_{T,p}$$

We cannot assume that the triple product term in the latter equation is zero. Hence, there are two limiting isobaric heat capacities; the equilibrium isobaric heat capacity $C_p(A = 0)$ and the frozen isobaric heat capacity $C_p(\xi eq)$. In other words, an isobaric heat capacity is not a strong function of state because it is concerned with a pathway between states. Unless otherwise stated, we use the symbol C_p to indicate an equilibrium transformation, $C_p(A = 0)$.

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1.14.57: Reversible Change

In thermodynamics the term 'reversible' means that in such a system the affinity for spontaneous change A is zero; we can in fact characterize the composition of the system by the symbol ξ^{eq}, indicating a time independent extent of chemical reaction. The composition of the system does not change because the affinity for spontaneous change is zero.

For a reversible change the affinity for spontaneous change is zero at all stages. The composition is represented by ξ^{eq}, and the rate of change $\mathrm{d}\xi^{\mathrm{eq}}/\mathrm{dt}$ is zero, at defined T and p. We represent the volume of the system using following equation.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \xi^{\mathrm{eq}}, \mathrm{A} = 0\right]$$

This equation means that the volume, a dependent variable, is unambiguously defined by the set of variables in the square brackets, [...]. The pressure is changed from p to $\mathrm{p} + \Delta\mathrm{p}$, such that the new equilibrium composition is $\xi + \Delta\xi$ where the affinity for spontaneous change is zero.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, (\mathrm{p} + \Delta\mathrm{p}), \xi^{\mathrm{eq}}(\mathrm{p} + \Delta\mathrm{p}), \mathrm{A} = 0\right]$$

Under these circumstances the change from $\mathrm{V}(\mathrm{p})$ to $\mathrm{V}(\mathrm{p} + \Delta\mathrm{p})$ is from one equilibrium state where $\mathrm{A} = 0$ to another equilibrium state where A is also zero. Such an equilibrium transformation is, in thermodynamic terms, reversible. All changes under the constraint that A remains at zero are reversible.

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1.14.58: Reversible Chemical Reactions

Two important themes in thermodynamics concern the description of chemical equilibria and the kinetics of chemical reactions in closed systems at fixed temperature and pressure. These two themes are often linked in descriptions of chemical reactions. We comment on this link.

A given aqueous solution (at temperature T and pressure p, which is close to the standard pressure, p^0) is prepared using chemical substance X. Spontaneous chemical reaction forms chemical substance Z in the following chemical reaction.

$$\mathrm{X(aq) \rightarrow Z(aq)}$$

Experiment confirms that the extent of chemical reaction is given by equation (b).

$$\frac{1}{\mathrm{V}}\frac{\mathrm{d}\xi}{\mathrm{dt}} = -\mathrm{k_1}\,[\mathrm{X}]$$

In this system, $\mathrm{c_x\{=[X]\}} = \mathrm{n_x/V}$. The common assumption is that for dilute solutions both $\mathrm{k_1}$ and volume V are independent of time.

$$\mathrm{dc_x/dt} = -\mathrm{k_1\,c_x}$$

Rate constant $\mathrm{k_1}$ is expressed using the unit, $\mathrm{s^{-1}}$. We consider a system prepared using chemical substance Z which undergoes spontaneous chemical reaction to form chemical substance X. The analogue of equation (c) takes the following form.;

$$\mathrm{dc_Z/dt} = -\mathrm{k_2\,c_Z}$$

We assert that the chemical reaction described by equations (c) and (d) proceed until the properties of the system (at fixed T and p) are independent of time. In other words the system is in thermodynamic equilibrium with the surroundings with $\mathbf{c}_X = \mathbf{c}_X^{eq}$ and $\mathbf{c}_Z = \mathbf{c}_Z^{eq}$ where, macroscopically, $\mathrm{dc_X/dt}$ and $\mathrm{dc_Z/dt}$ are zero. Also $\mathrm{limit\,(m_z \rightarrow 0; m_x \rightarrow 0)}\,\gamma_z = 1$ and $\mathrm{limit\,(m_x \rightarrow 0;\ and\ m_z = 0)}\,\gamma_x = 1$ Thus

$$\mathrm{k_1\,c_x^{eq} = k_2\,c_Z^{eq}}$$

From a thermodynamic point of view, at equilibrium (at fixed T and p) the affinity for spontaneous change A is zero, and the system is at a minimum in Gibbs energy G. If the molalities of substances X and Z are $\mathrm{m_X^{eq}}$ and $\mathrm{m_Z^{eq}}$ respectively, the standard increase in Gibbs energy $\mathrm{\Delta_r G^0(\ T, p, aq)}$ is related to a (dimensionless) thermodynamic equilibrium constant $\mathrm{K(aq; T; p)}$ using equation (f).

$$\mathrm{\Delta_r G^0 = -R\,T\,ln(K) = \mu_Z^0(aq) - \mu_x^0(aq)}$$

where,

$$\mathrm{K = \left(m_z\,\gamma_z/m^0\right)^{eq} / \left(m_x\,\gamma_x/m^0\right)^{eq}}$$

Here γ_X and γ_Z are the activity coefficients for solutes X and Z. If the aqueous solution is quite dilute, we can assume that the thermodynamic properties of the solution are ideal. Moreover the ratio $(m_Z/m_X)^{eq}$ is, based on the same approximation, equal to $(c_Z/c_X)^{eq}$. In other words equations (e) and (g) can be written in the following forms. Law of Mass Action

$$(c_Z/c_X)^{eq} = (k_1/k_2)^{eq}$$

Thermodynamics

$$\mathrm{(c_Z/c_X)^{eq} = K}$$

Within the context of the assumptions outlined above , we obtain by comparing equations (h) and (i) the following classic equation.

$$\mathrm{K = k_1/k_2}$$

Equation (j) is fascinating because the two sides of the equation have different origins, Law of Mass Action and the Laws of Thermodynamics. Indeed equation (j) is often used in an introduction to the concept of chemical equilibrium, the latter emerging as a ‘balance of rates of reaction’. In a wider context equation (j) is used in treatments of fast chemical reactions where a given closed

system is only marginally displaced from equilibrium by transient changes in electric field, magnetic field, pressure or temperature [1-3].

Footnotes

[1] E. Caldin, Fast Reactions in Solution, Blackwell Scientific Publications, Oxford, 1964.

[2] M. J. Blandamer, Introduction to Chemical Ultrasonics, Academic Press, London, 1973.

[3] The analysis takes a similar form in cases where the reaction stoichiometry is more complicated. Consider the case of an association reaction in aqueous solution.

$$\mathrm{X(aq) + Y(aq) \rightarrow Z(aq)}$$

Law of Mass Action For the forward reaction $\mathrm{dc_X/dt = -k_1\, c_X\, c_Y}$ For the reverse reaction

$$\mathrm{Z(aq) \rightarrow X(aq) + Y(aq)}$$

$$\mathrm{dc_Z/dt = -k_2\, c_z}$$

For a system where, macroscopically, $\mathrm{dc_X/dt = dc_Y/dt = dc_Z/dt = 0}$,

$$\mathrm{k_1\ (c_X\, c_Y)^{cq} = k_2\ (c_Z)^{eq}}$$

Or,

$$\mathrm{k_1/k_2 = (c_Z)^{eq} / (c_X\, c_Y)^{eq}}$$

From a thermodynamic viewpoint, at equilibrium (at fixed T and p),

$$\mathrm{\Delta_r G^0 = -R\, T\, \ln(K) = \mu_Z^0(aq) - \mu_X^0(aq) - \mu_Y^0(aq)}$$

where

$$\mathrm{K = \left(m_Z\, \gamma_Z/m^0\right)^{eq} / \left(m_X\, \gamma_X/m^0\right)^{eq}\ \left(m_Y\, \gamma_Y/m^0\right)^{eq}}$$

In the limit that the solution is dilute, $\mathrm{(\gamma_Z)^{eq} = (\gamma_x)^{eq} = (\gamma_Y)^{eq} = 1}$. Then

$$\mathrm{K = (c_Z/c_r)^{eq} / (c_X/c_r)^{eq}\ (c_Y/c_r)^{eq}}$$

Comparison of equations (e) and (h) allows identification of the ratio $\mathrm{k_1/k_2}$ with the equilibrium constant K.

Comment

If at equilibrium $\mathrm{dc_X/dt = 0}$ and $\mathrm{c_x^{cq} \neq 0}$ then according to equation (c), $\mathrm{k_1}$ must be zero. The same problem arises from equation (d). To circumvent this objection, the Principle of Microscopic Reversibility states that at Equilibrium, the amount of chemical substance X consumed by equation (a) and described by equation (c) equals the amount of chemical substance X produced by the reverse reaction described by equation (d).

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1.14.59: Salting-In and Salting-Out

A classic subject concerning the properties of salt solutions has centred for more than a century on the effects of an added salt on the solubility of an apolar (volatile) solute.

In terms of the Phase Rule, a given closed system contains two phases, gas and liquid. The liquid phase is an aqueous salt solution. A volatile chemical substance is distributed between the vapour and liquid phases. Hence the number of phases P equals 2; the number of components C equals 3; i.e. water + salt + volatile chemical substance. Hence the number of degrees of freedom F equals 3. If therefore we define the temperature, pressure and concentration of salt in the aqueous salt solution, the thermodynamic equilibrium is completely defined.

Similarly if the closed system contains pure liquid j and an aqueous salt solution which also contains solute j, the number of degrees of freedom is again 3. Then the equilibrium state is completely defined by specifying $\mathrm{T},\ \mathrm{p}$ and the concentration (molality) of salt in solution. In this case the equilibrium at defined T and p is defined by Equation 1.14.59.1.

$$\mu_{\mathrm{j}}^{*}(\ell) = \mu_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq}) \tag{1.14.59.1}$$

In the absence of salt, treating substance j as a solute in aqueous solution, Equation 1.14.59.2 describes this equilibrium in terms of the equilibrium composition of the solution assuming ambient pressure is close to the standard pressure.

$$\mu_{\mathrm{j}}^{*}(\ell) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right)_{\mathrm{aq}}^{\mathrm{eq}} \tag{1.14.59.2}$$

A similar equilibrium is established but this time the aqueous solution contains a salt, molality $\mathrm{m_s}$. Equation 1.14.59.2 takes the following form.

$$\mu_{\mathrm{j}}^{*}(\ell) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\ ln}\left(\mathrm{m_j}\,\gamma_{\mathrm{j}}/\mathrm{m}^{0}\right)_{\mathrm{s}}^{\alpha\mathrm{q}} \tag{1.14.59.3}$$

The subscript on the last term in Equation 1.14.59.3 indicates that the aqueous solution contains salt S as well as apolar solute j. According to equations 1.14.59.2 and 1.14.59.3, the two solubilities of substance j are related.

$$(m_j\,\gamma_j)_{aq}^{eq} = (m_j\,\gamma_j)_{s}^{eq} \tag{1.14.59.4}$$

Equation 1.14.59.4 is thermodynamically correct. The change in solubility of chemical substance j on adding salt S, molality ms is compensated by a change in the activity coefficient of solute j. The corresponding equation on the concentration scale has the form shown in Equation 1.14.59.5.

$$(c_j\,y_j)_{aq}^{eq} = (c_j\,y_j)_{s}^{eq} \tag{1.14.59.5}$$

The latter is the usual form of the equation. The analysis is readily repeated for the case where the chemical substance j is a volatile gas.

At this stage a number of extra-thermodynamic assumptions are built into the analysis. To reduce the clutter of symbols we drop the designation ‘eq’ taking this condition as implicit in all that follows. Further we assume that substance j is sparingly soluble so that in the aqueous solution $j-j$ solute-solute interactions are unimportant. Therefore the properties of solute j are ideal; $(\mathrm{y_j})_{\mathrm{aq}} = 1$. Hence from Equation 1.14.59.5,

$$\mathrm{ln}\left[(c_j)_{\mathrm{aq}}\,/\,(\mathrm{c_j})_{\mathrm{s}}\right] = \mathrm{ln}\left[(\mathrm{y_j})_{\mathrm{s}}\right] \tag{1.14.59.6}$$

In these terms $(\mathrm{y}_j)_{\mathrm{s}}$ is the activity coefficient of solute j in the aqueous salt solutions where the concentration of salt is represented by $\mathrm{c_s}$. For dilute salt solutions the assumption is made that $\mathrm{ln}\left[(\mathrm{y_j})_{\mathrm{s}}\right]$ is a linear function of $\mathrm{c_s}$.

$$\mathrm{ln}\left[(\mathrm{y_j})_{\mathrm{s}}\right] = \mathrm{k\,c_s} \tag{1.14.59.7}$$

Combination of equations 1.14.59.6 and 1.14.59.7 yields the following equation.

$$\mathrm{ln}\left[(c_j)_{aq}\,/\,(c_j)_{s}\right] = k\,c_s \tag{1.14.59.8}$$

Equation 1.14.59.8 is one form of the **Setchenow equation** in which constant k (at fixed T and p) is characteristic of salt S and solute j. An alternative form starts by expressing $(c_j)_s$ as $(c_j)_{aq} - \delta c_j$ implying a reduction in the solubility of solute j when a salt is

added; i.e. a salting-out.[2] Hence,

$$\delta c_j / (c_j)_{aq} = k\, c_s \qquad (1.14.59.9)$$

This Setchenow Equation requires that $\delta c_j / (c_j)_{aq}$ is a linear function of c_s. A positive k describes a salting-out; a negative k describes a salting-in. The phenomenon by which solubilities of gases in aqueous solutions are changed by adding a salt attracts enormous interest, both from practical and theoretical standpoints [3,4]. Conway reviewed theoretical models which attempt to account quantitatively for the phenomenon [5]. Considerable attention has been given to theories based on the relationship between the impact of the non-polar solute on the dielectric properties of the solvent and hence the chemical potential of the salt in solution [6,7].

For the most part salting-out is the commonly observed pattern [8]. Nevertheless there are some interesting cases where apolar solutes are salted-in by tetra-alkylammonium salts; benzene[9,10] , methane[11] and helium[12] in $Bu_4N^+\ Br^-(aq)$. It would appear that an added apolar solute is stabilized by interaction with the apolar alkyl groups of the cations [13].

Footnotes

[1] J.Setchenow, Z. Phys. Chem.,1889,**4**,117.

[2]

$$\ln\left[\frac{(c_j)_{aq}}{(c_j)_s}\right] = \ln\left[\frac{(c_j)_{aq}}{(c_j)_{aq} - \delta c_j}\right] = -\ln\left[\frac{(c_j)_{aq} - \delta c_j}{(c_j)_{aq}}\right]$$
$$-\ln\left[1 - \frac{\delta c_j}{(c_j)_{aq}}\right] \equiv \frac{\delta c_j}{(c_j)_{aq}}$$

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[4] For a review of the definitions of units used in this subject area see H. L. Clever, J. Chem. Eng. Data, 1983,**28**,340.

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m. Et_3N in $R_4NCl(aq)$; A. F. S. S. Mendonca, D. T. R. Formingo and I. M. S. Lampreia, J Solution Chem.,2002,**31**,653.
n. Et_3N in $CaCl_2(aq)$; A. F. S. S. Mendonca, D. T. R. Formingo and I. M. S. Lampreia, J Solution Chem.,2003,**32**,1033.

[9] Benzene in $R_4N^+\ Br^-(aq)$;J. E. Desnoyers, G. E. Pelletier and C. Jolicoeur, Can. J. Chem.,1965,**43**,3232.

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[11] RH in $R_4NBr(aq)$;W.-Y. Wen and J. H. Hung, J.Phys.Chem.,1970,**74**,170.

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1.14.60: Second Law of Thermodynamics

The Second Law introduces an extensive function of state, a property of a given system, called the **entropy**, symbol S.

Spontaneous chemical reaction in a closed system is driven by the affinity for spontaneous change A producing a change in chemical composition ξ. The change in entropy dS at temperature T is given by Equation 1.14.60.1.

$$\mathrm{T\,dS} = \mathrm{q} + \mathrm{A\,d}\xi \tag{1.14.60.1}$$

where

$$\mathrm{A\,d}\xi > 0 \tag{1.14.60.2}$$

The latter inequality is the LAW. This inequality is the key to chemistry. In effect the law states that if there is an affinity for a given chemical reaction (i.e. a driving 'force' for reaction) the chemical reaction will spontaneously proceed in that direction. This is the thermodynamic selection rule for which there are no exceptions.

In the limit that a system undergoes a 'reversible ' change, A is zero; the system is at equilibrium with the surroundings. For a reversible change

$$\mathrm{T\,dS} = \mathrm{q} \tag{1.14.60.3}$$

Often texts seek to answer the question 'what is entropy?' This is a fruitless task unless one draws attention to Equation 1.14.60.3 which reminds us that the product $\mathrm{T\,dS}$ is in fact a thermal energy. Chemists are familiar with spontaneous chemical reactions and Equations 1.14.60.1 and 1.14.60.2 present no conceptual problems [1].

Footnotes

[1] Robert Park, Voodoo Science, Oxford,2000. From page 7; 'The first law says you can't win; the second law says you can't even break even'. This comment is with respect to fraudulent claims of discoveries of perpetual motion machines.

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1.14.61: Solubility Products

A given closed system at temperature T and pressure p (which is close to ambient) contains an aqueous solution of a sparingly soluble salt MX; e.g. AgCl. The system also contains solid salt MX. When a soluble salt (e.g. $\mathrm{KNO_3}$) is added the solubility of salt MX increases. This remarkable observation is readily accounted for. The equilibrium involving the sparingly soluble salt is represented as follows.

$\mathrm{MX(s)}$	$\Leftrightarrow$	$\mathrm{M^+\ X^-(aq)}$
solid		solution

We represent the salt MX by the symbol j. At equilibrium,

$$\mu_{\mathrm{j}}''(\mathrm{s}) = \mu_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq})$$

In terms of the solubility S_j of the salt MX, a 1:1 salt,

$$\mu_{\mathrm{j}}^{*}(\ \mathrm{s}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + 2\,\mathrm{R\,T}\,\ln\left(\mathrm{S_j}\,\gamma_{\pm}/\mathrm{m^o}\right)$$

By definition

$$\Delta_{\mathrm{sol}}\,G^0 = -RT\,\ln K_s = \mu_j^0(aq) - \mu_j^*(s)$$

$\mathrm{K_S}$ is the solubility product, a characteristic property of salt MX (at defined T and p).

$$\mathrm{K_S} = \left[\mathrm{S_j}\,\gamma_{\pm}/\mathrm{m^0}\right]^2$$

Or,

$$\ln\left(\mathrm{S_j}/\mathrm{m^0}\right) = (1/2)\,\ln\left(\mathrm{K_s}\right) - \ln\left(\gamma_{\pm}\right)$$

According to the DHLL,

$$\ln\left(\gamma_{\pm}\right) = -S_{\gamma}\,\left(\mathrm{I}/\mathrm{m^0}\right)^{1/2}$$

I is the ionic strength of the solution which can be changed by adding a soluble salt. From equations (e) and (f),

$$\ln\left(\mathrm{S_j}/\mathrm{m^0}\right) = (1/2)\,\ln\left(\mathrm{K_s}\right) + \mathrm{S}_{\gamma}\,\left(\mathrm{I}/\mathrm{m^0}\right)^{1/2}$$

The key point to note is the positive sign in equation (g) showing that the theory accounts for the observed salting–in of the sparingly soluble salt. Further a plot of $\ln\left(S_j/m^0\right)$ against $\left(\mathrm{I}/\mathrm{m^0}\right)^{1/2}$ is linear yielding an estimate for $\mathrm{K_S}$ from the intercept.

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1.14.62: Solubilities of Gases in Liquids

Comparison of the solubilities of volatile chemical substance j in liquids ℓ_1 and ℓ_2 yields an estimate of the difference in reference chemical potentials, $\Delta\,(\ell_1 \rightarrow \ell_2)\,\mu_j^0(\,\mathrm{T})$.This is a classic subject [1-10] with two consequences.

i. A vast amount of information has been published, not all, unfortunately, of high quality.
ii. Many terms and definitions have been developed. Determination of thermodynamic parameters characterizing gaseous solubilities is not straightforward. Account has to be taken of the fact that the properties of real gases are not perfect.

A closed system contains two phases, liquid and gaseous, at temperature T. The liquid is water; a sparingly soluble chemical substance j exists in both gas and liquid phases. A phase equilibrium is established for substance j in the two phases. In terms of the Phase Rule, there are two phases and two components. Hence there are two degrees of freedom. If the temperature and pressure are defined, the compositions of the two phases are fixed. In terms of chemical potentials with reference to substance j the following condition holds.

$$\mu_j^{eq}\,(\mathrm{aq};\mathrm{x_j},\mathrm{p},\mathrm{T}) = \mu_j^{eq}\,(\mathrm{g};\mathrm{p_j},\mathrm{T})$$

Here p_j is the equilibrium partial pressure of substance j in the gas phase at pressure p where pressure p equals $(\mathrm{p}_j + \mathrm{p}_1)^{eq}$ where p_1 is the equilibrium partial pressure of water in the vapor phase. Equation (a) establishes the thermodynamic basis of the phenomenon discussed here. However historical and practical developments resulted in quite different approaches to the description of the solubilities of gases in liquids. The thermodynamic treatment is not straightforward if we recognize that the thermodynamic properties of the vapor (i.e. gas phase) and the solution are not ideal. When both the solubility and the partial pressure of the 'solute' in the gas phase are low, the assumption is often made that the thermodynamic properties of gas and solution are ideal. Then the analysis of solubility is reasonably straightforward [1-3]. In a sophisticated analysis, account must be taken of the intermolecular interactions in the vapor phase and solute-solute interactions in solution [4-10]. We review the basis of analyses where the thermodynamic properties of gas and liquid phases are ideal. Nevertheless equation (a) is the common starting point for the analysis.

Bunsen Coefficient, α

By definition, the Bunsen Coefficient α is the volume of a gas at $273.15\ \mathrm{K}$ and standard pressure p^0 which dissolves in unit volume of a solvent when the partial pressure of the gas equals p^0. Experiment yields the volume $\mathrm{V}_j(\mathrm{g})$ of gas j at temperature T and partial pressure p_j absorbed by volume $\mathrm{V_s}$ of solvent at temperature T. The volume of gas at $273.15\ \mathrm{K}$ and standard pressure p^0, $\mathrm{V_j}\,(\mathrm{g};\mathrm{p}^0;273.15\ \mathrm{K})$ is given by equation (b) assuming that gas j has the properties of a perfect gas.

$$\mathrm{V_j}\,(\mathrm{g};\mathrm{p}^0;273.15\ \mathrm{K}) = [\mathrm{p_j}\,\mathrm{V_j}\,(\mathrm{g};\mathrm{T};\mathrm{p_j})\ 273.15\ \mathrm{K}/\mathrm{p}^0\,\mathrm{T}]$$

Hence experiment yields the ratio, $[\mathrm{V_j}\,(\mathrm{g};\mathrm{T};\mathrm{p_j})\,/\mathrm{V_s}(\ell;\mathrm{T};\mathrm{p})]$. By simple proportion we obtain the volume, $\mathrm{V_j}\,(\mathrm{g};\mathrm{p}^0;273.15\ \mathrm{K})$ in the event that the gas j was at pressure p^0 above the liquid phase. Bunsen coefficient,

$$\alpha = \frac{\mathrm{V_j}\,(\mathrm{g};\mathrm{T};\mathrm{p_j})}{\mathrm{V_s}(\ell;\mathrm{T};\mathrm{p})}\left(\frac{\mathrm{p_j}}{\mathrm{p}^0}\right)\frac{273.15\ \mathrm{K}}{\mathrm{T}}$$

At ambient pressure, if the partial pressure of the solvent is negligibly small,

$$\alpha = \frac{\mathrm{V_j}(\mathrm{g};\mathrm{T};\mathrm{p})}{\mathrm{V_s}(\ell;\mathrm{T};\mathrm{p})}\left(\frac{273.15\ \mathrm{K}}{\mathrm{T}}\right)$$

The assumption that substance j is a perfect gas can be debated but the correction is often less that 1%.

Oswald Coefficient

A given closed system comprises gaseous and liquid phases, at temperature T. The system is at equilibrium such that equation (a) holds. We assume that the thermodynamic properties of the solution and the gas phase are ideal and that an equilibrium exists for chemical substance j between the two phases. The solution is at pressure p^0, standard pressure which is close to ambient pressure.

$$\mu_j^0\,(\ \mathrm{g};\mathrm{id};\mathrm{T};\mathrm{p}^0) + \mathrm{R\,T\,ln}\,(\mathrm{p_e^{eq}}/\mathrm{p}^0) = \mu_j^0\,(\ \mathrm{s\,ln};\mathrm{id};\mathrm{T};\mathrm{p}^0) + \mathrm{R\,T\ ln}\,(\mathrm{c_j}/\mathrm{c_r})$$

For a perfect gas,

$$\mathrm{p_j\,V_j(g) = n_j\,R\,T}$$

For a solution,

$$\mathrm{c_j = n_j/V(aq)}$$

In these terms $\mathrm{V(aq)}$ is the volume of solution which dissolves n_j moles of chemical substance j from the gas phase.

$$\mu_j^0\,(\,\mathrm{g;id;T;p^0}) + \mathrm{R\,T\,ln}\left(\frac{\mathrm{n_j\,R\,T}}{\mathrm{V_j(g)}}\,\frac{1}{\mathrm{p^0}}\right) = \mu_j^0\,(\,\mathrm{s\,ln;id;T;p^0}) + \mathrm{R\,T\,ln}\left(\frac{\mathrm{n_j}}{\mathrm{V(aq)}}\,\frac{1}{\mathrm{c_r}}\right)$$

The Ostwald Coefficient L is defined in terms of reference chemical potentials of substance j in solution and gas phase.

$$\Delta_{s\,\mathrm{ln}}\mathrm{G^0}\,(\,\mathrm{T,p^0}) = -\mathrm{R\,T\,ln(L)} = \mu_j^0\,(\,\mathrm{s\,ln;id;T;p^0}) - \mu_j^0\,(\,\mathrm{g;id;T;p^0})$$

From equation (h),

$$\Delta_{s\,\mathrm{ln}}\mathrm{G^0}\,(\,\mathrm{T,p^0}) = \mathrm{R\,T\,ln}\left[\frac{\mathrm{n_j\,R\,T}}{\mathrm{V_j(g)}}\,\frac{\mathrm{V(aq)\,c_r}}{\mathrm{n_j\,p^0}}\right]$$

$$\Delta_{s\,\mathrm{ln}}\mathrm{G^0}\,(\,\mathrm{T,p^0}) = \mathrm{R\,T\,ln}\left[\frac{\mathrm{V(aq)}}{\mathrm{V_j(g)}}\,\frac{\mathrm{R\,T\,c_r}}{\mathrm{p^0}}\right]$$

Because $\mathrm{V(aq)}$ and $\mathrm{V}_j\mathrm{(g)}$ are expressed in the same units, the Oswald coefficient is dimensionless. The key assumption is that the thermodynamic properties of gas and solution phases are ideal.

Ostwald coefficients can be defined in several ways [4]. In the analysis set out above we refer to the volume of the solution containing solvent and solute j. Another definition refers to the volume of pure liquid which dissolves a volume of gas V_j.

$$\mathrm{L^0 = [V_g/V^*(\ell)]^{eq}}$$

A third definition refers to ratio of concentrations of substances j in liquid and gas phases.

$$\mathrm{L_c = \left[c_j^L/c_j^V\right]^{eq}}$$

In effect an Oswald coefficient describes an equilibrium distribution for a volatile solute between gas phase and solution. The Oswald coefficient is related to the (equilibrium) mole fraction of dissolved gas, x_j using equation (n) where p_j is the partial pressure of chemical substance j and $\mathrm{V}_1^*(\ell)$ is the molar volume of the solvent [11].

$$\mathrm{x_2 = \{[R\,T/L\,p_j\,V_1^*(\ell)] + 1\}^{-1}}$$

Henry's Law Constant

In a given closed system at temperature T, gas and solution phases are in equilibrium. The thermodynamic properties of both phases are ideal. Then according to Henry's Law, the partial pressure of volatile solute j is a linear function of the concentration c_j at fixed temperature.

$$\mathrm{p_j(vap) = K_c\,c_j/c_r}$$

$\mathrm{K_c}$ is the Henry's Law constant (on the concentration scale), characteristic of solvent, solute and temperature. Similarly on the mole fraction scale,

$$\mathrm{p_j(vap) = K_x\,x_j}$$

This subject, gas solubilities, is enormously important. We draw attention to some interesting reports concerning solubilities with particular reference to aqueous solutions and the environment [12].

Footnote

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[11]

$$\frac{n_j\,R\,T}{V_j(g)}\,\frac{V(aq)\,c_r}{n_j\,p^0} = \frac{[mol]\;[JK^{-1}\;mol^{-1}]\;[K]}{[m^3]}\,\frac{[m^3]\;[molm^{-3}]}{[mol]\;[Nm^{-2}]}$$
$$= \frac{[Nm]}{[m^3]}\,\frac{1}{[\,Nm^{\,-2}]} = [1]$$

For a perfect gas j,

$$p_j\,V_j(g) = n_j\,R\,T$$

$$V_j(g) = n_j\,RT/p_j$$

For n_1 moles of liquid 1, density $\rho_1^*(\ell)$,

$$n_1\,V_1^*(\ell) = n_1\,M_1/\rho_1^*(\ell)$$

By definition, at temperature T,

$$L = V_j(g)/V_1^*(\ell)$$

$$L = \frac{n_j\,R\,T}{p_j}\,\frac{\rho_1^*(\ell)}{n_1\,M_1}$$

Hence,

$$\frac{n_1}{n_j} = \frac{R\,T}{L\,p_j}\,\frac{\rho_1^*(\ell)}{M_1} = \frac{R\,T}{L\,p_j\,V_1^*(\ell)}$$

But mole fraction of solute j in solution,

$$x_j = \frac{n_j}{n_1 + n_j} = \frac{1}{(n_1/n_j) + 1}$$

From equations (f) and (g),

$$x_j = [\{R\,T/L\,p_j\,V_1^*(\ell)\} + 1]^{-1}$$

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1.14.63: Solubilities of Solids in Liquids

This very large subject can be divided into two groups. The first group concerns the solubility of a given solid substance j in a given solvent, liquid ℓ_1. The second group involves comparison of the solubilities of a given solid in two liquids, ℓ_1 and ℓ_2.

A closed system (at defined T and p, the latter being close to the standard pressure) contains solid substance j in equilibrium with an aqueous solution containing solute j. The system is characterized by the (equilibrium) solubility, $\mathrm{m_j^{eq}(aq)}$. At equilibrium,

$$\mu_{\mathrm{j}}^{*}(\mathrm{\ s}) = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) + \mathrm{R\,T\ ln}\left[\mathrm{m_j^{eq}(aq)}\,\gamma_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq})/\mathrm{m}^{0}\right]$$

Then

$$\Delta\mu_{\mathrm{j}}^{0} = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) - \mu_{\mathrm{j}}^{*}(\mathrm{\ s}) = -\mathrm{R\,T\ ln}\left[\mathrm{m_j^{eq}(aq)}\,\gamma_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq})/\mathrm{m}^{0}\right]$$

If the aqueous solution is dilute and the solubility is low, it can often be assumed that the properties of the solution are ideal. Hence,

$$\Delta\mu_{\mathrm{j}}^{0} = \mu_{\mathrm{j}}^{0}(\mathrm{aq}) - \mu_{\mathrm{j}}^{*}(\mathrm{s}) = -\mathrm{R\,T\ ln}\left[\mathrm{m_j^{eq}(aq)}/\mathrm{m}^{0}\right]$$

It should be noted that the sign of $\Delta\mu_j^0$ depends on whether or not $m_j^{eq}(aq)$ is larger or less than unity.

We illustrate the second approach by considering a combination of the experiment described above and an experiment where the solvent is a binary aqueous mixture, mole fraction composition $\mathrm{x_2}$. At equilibrium,

$$\mu_j^*(s) = \mu_j^0\,(s\,\mathrm{ln};x_2) + RT\ \mathrm{ln}\left[m_j^{\mathrm{eq}}\,(s\,\mathrm{ln};x_2)\ \gamma_j^{\mathrm{eq}}\,(s\,\mathrm{ln};x_2)\,/m^0\right]$$

$$\Delta\,(\mathrm{aq}\rightarrow \mathrm{x_2})\,\mu_{\mathrm{j}}^{0} = \mu_{\mathrm{j}}^{0}\,(\mathrm{\ s\,ln;x_2}) - \mu_{\mathrm{j}}^{0}(\mathrm{aq})$$
$$= -\mathrm{R\,T\ ln}\left[\mathrm{m_j^{eq}}\,(\mathrm{s\,ln;x_2})\ \gamma_{\mathrm{j}}^{\mathrm{eq}}\,(\mathrm{s\,ln;x_2})\,/\mathrm{m_j^{eq}(aq)}\,\gamma_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq})\right]$$

If both solutions are dilute in substance j, the ratio, $\gamma_j^{\mathrm{eq}}\,(\mathrm{s\,ln;x_2})\,/\gamma_{\mathrm{j}}^{\mathrm{eq}}(\mathrm{aq})$ can be assumed to be close to unity. In fact this is a better approximation than assuming both activity coefficients are unity. Then

$$\Delta\,(\mathrm{aq}\rightarrow \mathrm{x_2})\,\mu_{\mathrm{j}}^{0} = -\mathrm{R\,T\ ln}\left[\mathrm{m_j^{eq}}\,(\mathrm{s\,ln;x_2})\,/\mathrm{m_j^{eq}(aq)}\right]$$

In other words if the solubility of substance j increases on adding solvent component 2 then $\Delta\,(\mathrm{aq}\rightarrow \mathrm{x_2})\,\mu_{\mathrm{j}}^{\mathrm{c}}$ is negative. This stabilization is a consequence of a difference in solute-solvent interactions.

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1.14.64: Solutions: Solute and Solvent

A given solution (at temperature T and pressure p, where the latter is close to the standard pressure) is prepared using $1\ \mathrm{kg}$ of water(ℓ) and m_j moles of a simple solute. The Gibbs energy $\mathrm{G}\left(\mathrm{w}_1 = 1\ \mathrm{kg}\right)$ is given by equation (a).

$$\mathrm{G}\left(\mathrm{w}_1 = 1\ \mathrm{kg}\right) = \left(1/\mathrm{M}_1\right)\ \left[\mu_1^*(\ell) - \phi\,\mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}\right] + \mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\ \ln\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right)\right]$$

In the event that the thermodynamic properties of the solution are ideal,

$$\mathrm{G}\left(\mathrm{w}_1 = 1\ \mathrm{kg};\mathrm{id}\right) = \left(1/\mathrm{M}_1\right)\ \left[\mu_1^*(\ell) - \mathrm{R}\,\mathrm{T}\,\mathrm{M}_1\,\mathrm{m_j}\right] + \mathrm{m_j}\ \left[\mu_\mathrm{j}^0(\mathrm{aq}) + \mathrm{R}\,\mathrm{T}\ \ln\left(\mathrm{m_j}/\mathrm{m}^0\right)\right]$$

The excess Gibbs energy G^E for the solution prepared using $1\ \mathrm{kg}$ of water(ℓ) is given by equation (c).

$$\mathrm{G}^\mathrm{E} = \mathrm{G}\left(\mathrm{w}_1 = 1\ \mathrm{kg}\right) - \mathrm{G}\left(\mathrm{w}_1 = 1\ \mathrm{kg};\mathrm{id}\right)$$

Therefore [1]

$$\mathrm{G}^\mathrm{E} = \mathrm{R}\,\mathrm{T}\,\mathrm{m_j}\ \left[1 - \phi + \ln\left(\gamma_\mathrm{j}\right)\right]$$

Hence at fixed T and p, the dependence of G^E on m_j is given by equation (e).

$$\left(1/\mathrm{R}\,\mathrm{T}\right)\mathrm{dG}^\mathrm{E}/\mathrm{dm_j} = 1 - \phi + \ln\left(\gamma_\mathrm{j}\right) - \mathrm{m_j}\,\mathrm{d}\phi/\mathrm{dm_j} + \mathrm{m_j}\,\mathrm{d}\ln\left(\gamma_\mathrm{j}\right)/\mathrm{dmj_j}$$

According to the Gibbs-Duhem equation, the chemicals potentials of solvent $\mu_1(\mathrm{aq})$ and solute $\mu_j(\mathrm{aq})$ are linked. At fixed T and p,

$$\mathrm{n}_1\,\mathrm{d}\mu_1(\mathrm{aq}) + \mathrm{n_j}\,\mathrm{d}\mu_\mathrm{j}(\mathrm{aq}) = 0$$

Then for a solution prepared using $1\ \mathrm{kg}$ of water(ℓ),

$$\left(1/M_1\right)\ d\mu_1(aq) + m_j\,d\mu_j(aq) = 0$$

In terms of the impact of adding dm_j moles of solute,

$$\left(1/M_1\right)\ d\mu_1(aq)/dm_j + m_j\,d\mu_j(aq)/dm_j = 0$$

The Gibbs-Duhem relation describes moderation of the effects of added dm_j moles of solute j on the changes in chemical potentials of solute and solute. We use the equation which relates these chemical potentials to the composition of the solution. For simple solutes (e.g. urea) at ambient pressure, equation (g) takes the following form.

\[\begin{aligned}
&{\left[1 / \mathrm{M}_{1}\right] \, \mathrm{d}\left[\mu_{1}^{*}(\ell)-\phi \, \mathrm{R} \, \mathrm{T} \, \mathrm{M}_{1} \, \mathrm{m}_{\mathrm{j}}\right]} \\
&\quad+\mathrm{m}_{\mathrm{j}} \, \mathrm{d}\left[\mu_{\mathrm{j}}^{0}(\mathrm{aq})+\mathrm{R} \, \mathrm{T} \, \ln \left(\mathrm{m}_{\mathrm{j}} \, \gamma_{\mathrm{j}} / \mathrm{m}^{0}\right]=0\right.
\end{aligned} \nonumber \]

Hence,

$$\mathrm{d}\left[-\phi\,\mathrm{m_j}\right] + \mathrm{m_j}\ \left[\mathrm{d}\ln\left(\mathrm{m_j}\,\gamma_\mathrm{j}/\mathrm{m}^0\right] = 0$$

The simple differential equation (j) is important in developing links between the thermodynamic properties of solutions, solvent and solute. The integrated form of this equation is important. From equation (j),

$$\mathrm{d}\left[-\phi\,\mathrm{m_j}\right] + \mathrm{m_j}\,\mathrm{d}\ln\left(\mathrm{m_j}\right) + \mathrm{m_j}\,\mathrm{d}\ln\left(\gamma_\mathrm{j}\right) = 0$$

Therefore,

$$-\phi\,dm_j - m_j\,d\phi + dm_j + m_j\,d\ln\left(\gamma_j\right) = 0$$

Or,

$$m_j \, d \ln (\gamma_j) = (\phi - 1) \, dmm_j + m_j \, d\phi$$

Or, with a slight re-arrangement,

$$d \ln (\gamma_j) = d\phi + (\phi - 1) \, d \ln (m_j)$$

Hence we obtain an equation for $\ln (\gamma_j)$ in terms of the dependence of $(\phi - 1)$ on molality of solute bearing in mind that $\ln (\gamma_j)$ equals zero and ϕ equals 1 at $m_j = 0$.

$$\ln (\gamma_j) = (\phi - 1) + \int_o^{m_j} (\phi - 1) \, d \ln (m_j)$$

In another approach we start again with equation (j).

$$d [\phi \, m_j] = m_j \, d \left[\ln \left(m_j / m^0 \right) \right] + m_j \, d [\ln (\gamma_j)]$$

Or,

$$d [\phi \, m_j] = m_j \, d \left[\ln (m_j) - \ln \left(m^0 \right) \right] + m_j \, d [\ln (\gamma_j)]$$

Or,

$$d [\phi \, m_j] = dm_j + m_j \, d [\ln (\gamma_j)]$$

Following integration from '$m_j = 0$' to m_j,

$$\phi \, m_j = m_j + \int_0^{m_j} m_j \, d \ln (\gamma_j)$$

$$\phi = 1 + (1/m_j) \int_0^{m_j} m_j \, d \ln (\gamma_j)$$

$$\phi - 1 = (1/m_j) \int_0^{m_j} m_j \, d \ln (\gamma_j)$$

In other words $(\phi - 1)$ is related to the integral of $m_j \, d \ln (\gamma_j)$ between the limits '$m_j = 0$' and m_j. Equation (e) can be re-expressed as an equation of $\ln (\gamma_j)$.

$$\ln (\gamma_j) = -(1 - \phi) + m_j \, d\phi / dm_j - m_j \, d \ln (\gamma_j) / dm_j + (1/R \, T) \, dG^E / dmj_j$$

Hence from equation (r),

$$m_j \, d\phi + \phi \, dmj_j = dmm_j + m_j \, d [\ln (\gamma_j)]$$

Or,

$$m_j \, d\phi / dmm_j + \phi - 1 - m_j \, d \ln (\gamma_j) / dmm_j = 0$$

Or,

$$-(1 - \phi) + m_j \, d\phi / dm_j - m_j \, d \ln (\gamma_j) / dmm_j = 0$$

Then with reference to equation (v), [2]

$$\ln (\gamma_j) = (1/R \, T) \, dG^E / dm_j$$

Combination of equations (z) and (d) yields an equation for $(1 - \phi)$ in terms of G^E. Thus

$$G^E / R \, T = m_j \, (1 - \phi) + (m_j / R \, T) \; dG^E / dm_j$$

Or [3],

$$(1 - \phi) = (1/R \, T) \; \left[G^E / m_j - dG^E / dm_j \right]$$

Or,

$$(1 - \phi) = - \, (m_j / R \, T) \; \left\{ d \left[G^E / m_j \right] / dm_j \right\}$$

Footnotes

[1]

$$\mathrm{G^E} = \left[\mathrm{JK^{-1}\ mol^{-1}}\right]\ [\mathrm{K}]\ \left[\mathrm{molkg^{-1}}\right]\ [1] = \left[\mathrm{Jkg^{-1}}\right]$$

[2]

$$\ln\left(\gamma_{\mathrm{j}}\right) = \frac{1}{\left[\ \mathrm{J\ K^{-1}\ mol^{-1}}\right]\ [\mathrm{K}]}\ \frac{\left[\mathrm{Jkg^{-1}}\right]}{\left[\mathrm{molkg^{-1}}\right]} = [1]$$

[3]

$$(1-\phi) = \left[\frac{[1]}{\left[\mathrm{JK^{-1}\ mol^{-1}}\right]\ [\mathrm{K}]}\right]\ \left[\frac{\left[\mathrm{Jkg^{-1}}\right]}{\left[\mathrm{molkg^{-1}}\right]}\right] = [1]$$

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1.14.65: Spontaneous Change: Isothermal and Isobaric

By definition,

$$\mathrm{G} = \mathrm{H} - \mathrm{T}\,\mathrm{S}$$

$\mathrm{G},\ \mathrm{H}$ and S are extensive functions of state. At fixed T and p, the dependences of these variables on extent of reaction, ξ are related.

$$(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}} = (\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}} - \mathrm{T}\,(\partial \mathrm{S}/\partial \xi)_{\mathrm{T,p}}$$

For a spontaneous change $(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}} < 0$ where the affinity for spontaneous change $\mathrm{A}\,[= -(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}}]$ is positive. This can arise under two limiting circumstances.

a. The spontaneous process is exothermic; [i.e.[i.e. $(\partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}} < 0$] such that $|\mathrm{T}\,(\partial \mathrm{S}/\partial \xi)_{\mathrm{T,p}}| < |\ \partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}\ |$. The decrease in G is enthalpy driven.
b. The spontaneous process is endothermic; [i.e. $(\partial H/\partial \xi)_{\mathrm{T,p}} > 0$] such that $|\mathrm{T}\,(\partial \mathrm{S}/\partial \xi)_{\mathrm{T,p}}| > |\ \partial \mathrm{H}/\partial \xi)_{\mathrm{T,p}}\ |$. The decrease in G is entropy driven.

If for a given possible process, $(\partial G/\partial \xi)_{\mathrm{T,p}} > 0$, then the process is not spontaneous; there is no affinity for spontaneous change. If $(\partial \mathrm{G}/\partial \xi)_{\mathrm{T,p}}$ is zero at defined T and p, the system is at equilibrium with the surroundings; the affinity for spontaneous change is zero. The chemical equilibrium is stable if $(\partial \mathrm{A}/\partial \xi)_{\mathrm{T,p}}$ is negative.

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1.14.66: Spontaneous Chemical Reaction

A closed reaction vessel at $298.2\ \mathrm{K}$ and $101325\ \mathrm{Nm^{-2}}$ is filled with a solution having the initial composition, water ($1.2\ \mathrm{mol}$), $\mathrm{NaOH(aq, 0.5\ mol)}$, $\mathrm{CH_3.COOC_2H_5(aq, 0.2\ mol)}$. Experiment shows that the system spontaneously changes composition. We write the overall chemical reaction as:

$$\mathrm{CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH}$$

In this connection we state that the reaction is driven by the affinity for spontaneous reaction leading to a change in chemical composition characterized by the extent of reaction, ξ.

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1.14.67: Standard States: Reference States: Processes

- Pressure:
  - [1] standard pressure \(10^{5} \mathrm{~N m}^{-2}
- States:
  - Solids:
    - pure solids
  - Liquids:
    - pure liquids
  - Gases:
    - ideal gas at standard pressure
- Solutions:
  - Simple Solution
  - Solvent: pure liquid
  - Solute: ideal solution at unit molality; $1\ \mathrm{molkg}^{-1}$
- Process/Change [2,3,4] $\Delta_{\mathrm{proc}}\ X^{0}$
- Subscript 'proc' indicates the process. Examples include
  - $\mathrm{f} =$ formation
  - $\mathrm{c} =$ combustion
  - $\mathrm{vap} =$ vaporisation
  - $\mathrm{r} =$ chemical reaction
  - $\mathrm{soln} =$ solution]
  - $\neq =$ activation; an attempt to represent the classic double dagger symbol suggested by Eyring . The symbol is written as a superscript; e.g. $\Delta^{\neq}V^{0} =$ standard volume of activation.
- Example; $\Delta_{\mathrm{c}}\mathrm{H}^{0} =$ standard enthalpy of combustion.

Footnotes

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1.14.68: Surroundings and System

System

The word ‘system’ describes that part of the universe which we have identified for the purpose of studying its chemical properties. The term "universe" in the latter sentence is somewhat pretentious (= implying ‘of enormous importance’ in a way that is doubtful). From the practical point of view, a chemist identifies the system as the contents of the reaction vessel (flask) under investigation.

Surroundings

The rest of the universe comprises the surroundings. We as observers of the properties plus all our measuring equipment including spectrophotometers and calorimeters are part of the surroundings. As far as chemists are concerned the surroundings mean the laboratory (+ chemist!) surrounding the system.

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1.14.69: Temperature of Maximum Density: Aqueous Solutions

At ambient pressure, the molar volume of water (ℓ) is a minimum near 277 K, the temperature of maximum density, TMD. The TMD is sensitive to the concentration and nature of added solute. Generally added salts lower the TMD, the extent of lowering being often written $\Delta\theta$. For dilute salt solutions, TMD is a linear function of the molality of salt, m_j,$(\partial\Delta\theta/\partial m_\mathrm{j})$ being negative; Despretz Law. However considerable interest is generated by the observation that some organic solutes at low mole fractions raise the TMD; i.e. $\Delta\theta > 0$; e.g. 2-methylpropan-2-ol.

Although the phenomenon of a shift in TMD is straightforward from an experimental standpoint, explanations distinguish between possible contributions to the shift in TMD. Most treatments identify two contributions to the shift in TMD, an 'ideal' shift and a contribution which reflects the fact that the thermodynamic properties of the aqueous system are not ideal [1,2].

At the outset we assume that the molar volume of water at ambient pressure in the region of the TMD is a quadratic function of the difference ($\mathrm{T} - \mathrm{TMD}^*$) where TMD^* is the temperature of maximum density of water (ℓ) [2]. At temperature T the molar volume $\mathrm{V}_1^*(\ell, \mathrm{T})$ is given by equation (a) where χ_1 is a dimensionless property of water (ℓ) [3].

$$\mathrm{V}_1^*(\ell, \mathrm{T}) = \mathrm{V}_1^*(\ell, \mathrm{TMD}^*) \left\{1 + \chi_1 \left(\mathrm{T} - \mathrm{TMD}^*\right)^2 / [\mathrm{K}]^2\right\}$$

We consider briefly three types of systems;

i. binary aqueous mixtures,
ii. aqueous solutions, and
iii. aqueous salt solutions.

(i) Binary Aqueous Mixtures

For the non-aqueous component, the dependence of molar volume $\mathrm{V}_2^*(\ell, \mathrm{T})$ on temperature is given by equation (b) where χ_2 is a dimensionless property of the non-aqueous component.

$$\mathrm{V}_2^*(\ell, \mathrm{T}) = \mathrm{V}_2^*(\ell, \mathrm{TMD}^*) \left\{1 + \chi_2 \left(\mathrm{T} - \mathrm{TMD}^*\right) / [\mathrm{K}]\right\}$$

$\mathrm{V}_2^*(\ell, \mathrm{TMD}^*)$ is the molar volume of non-aqueous component at the temperature TMD^*. The volume of a mixture prepared using n_1 and n_2 moles of the two liquids at temperature θ under the no-mix condition is given by equation (c).

$$\mathrm{V}(\mathrm{no-mix}; \theta) = \mathrm{n}_1 \mathrm{V}_1^*(\ell; \theta) + \mathrm{n}_2 \mathrm{V}_2^*(\ell; \theta)$$

Hence,

$$\begin{aligned}\mathrm{V}(\mathrm{no-mix}; \theta) = \mathrm{n}_1 &\left[\mathrm{V}_1^*(\ell; \mathrm{TMD}^*) \left\{1 + \chi_1 \left(\theta - \mathrm{TMD}^*\right)^2 / [\mathrm{K}]^2\right\}\right] \\ &+ \mathrm{n}_2 \left[\mathrm{V}_2^*(\ell; \mathrm{TMD}^*) \left\{1 + \chi_2 \left(\theta - \mathrm{TMD}^*\right) / [\mathrm{K}]\right\}\right]\end{aligned}$$

At temperature θ, the volume of the real mixture $\mathrm{V}(\mathrm{mix}; \theta)$ is given by equation (e) where $\mathrm{V}_1(\mathrm{mix}; \theta)$ and $\mathrm{V}_2(\mathrm{mix}; \theta)$ are the partial molar volumes of the two components in the mixture at temperature θ.

$$\mathrm{V}(\mathrm{mix}; \theta) = \mathrm{n}_1 \mathrm{V}_1(\mathrm{mix}; \theta) + \mathrm{n}_2 \mathrm{V}_2(\mathrm{mix}; \theta)$$

The volume of mixing at temperature θ is given by equation (f). By definition,

$$\Delta_\mathrm{mix} V(\theta) = V(\mathrm{mix}; \theta) - V(\mathrm{\ no\ -mix}; \theta)$$

Hence,

$$\begin{aligned}\Delta_\mathrm{mix} \mathrm{V}(\theta) = &\mathrm{n}_1 \left\{\mathrm{V}_1(\mathrm{mix}; \theta) - \mathrm{V}_1^*(\ell; \mathrm{TMD}^*) \left[1 + \chi_1 \left(\theta - \mathrm{TMD}^*\right)^2 / [\mathrm{K}]^2\right]\right\} \\ &+ \mathrm{n}_2 \left\{\mathrm{V}_2(\mathrm{mix}; \theta) - \mathrm{V}_2^*(\ell; \mathrm{TMD}^*) \left[1 + \chi_2 \left(\theta - \mathrm{TMD}^*\right) / [\mathrm{K}]\right]\right\}\end{aligned}$$

But the molar volume of mixing at temperature θ,

$$\Delta_\mathrm{mix} \mathrm{V}_\mathrm{m}(\theta) = \Delta_\mathrm{mix} \mathrm{V}(\theta) / \left(\mathrm{n}_1 + \mathrm{n}_2\right)$$

Hence,

$$\Delta_{\text{mix}}\mathrm{V_m}(\theta) = \mathrm{x_1\,V_1(mix;\theta) + x_2\,V_2(mix;\theta)}$$
$$-\left\{\mathrm{x_1\,V_1^*(\ell;TMD)}\,\left[1+\chi_1\,(\theta-\mathrm{TMD^*})^2/[\mathrm{K}]^2\right]\right\}$$
$$-\left\{\mathrm{x_2\,V_2^*(\ell;TMD^*)}\,\left[1+\chi_2\,(\theta-\mathrm{TMD^*})/[\mathrm{K}]\right]\right\}$$

Then the differential of $\Delta_{\text{mix}}\ \mathrm{V_m}$ is given by equation (j).

$$\begin{aligned}\mathrm{d}\Delta_{\text{mix}}\mathrm{V_m(T)} =& \mathrm{x_1\,dV(mix;T) + V_1(mix;T)\,dx_1}\\ &+\mathrm{x_2\,dV_2(mix;T) + V_2(mix;T)\,dxx_2}\\ &-\mathrm{V_1^*(\ell;TMD^*)}\,\left[1+\chi_1\,(\mathrm{T-TMD})^2\,[\mathrm{K}]^{-2}\right]\,\mathrm{dx}\\ &-\mathrm{x_1\,V_1^*(\ell;TMD)}\,2\,\chi_1\,(\mathrm{T-TMD^*})\,[\mathrm{K}]^{-2}\right]\,\mathrm{dT}\\ &-\mathrm{V_2^*(\ell;TMD^*)}\,\left[1+\chi_1\,(\mathrm{T-TMD})^2\,[\mathrm{K}]^{-2}\right]\,\mathrm{dx_2}\\ &-\mathrm{x_2\,V_2^*(\ell;TMD)}\,\chi_2\,[\mathrm{K}]^{-1}\,\mathrm{dT}\end{aligned}$$

But according to the Gibbs-Duhem Equation, at fixed pressure

$$x_1\,dV_1(\mathrm{mix};T) + x_2\,dV_2(\mathrm{mix};T) = E_{pm}(\mathrm{mix};T)\,dT$$

In equation (k), $\mathrm{E_{pm}(mix;T)}$ is the molar isobaric expansion of the mixture. Equation (j) can therefore be reorganized into equation (l).

$$\begin{aligned}&\mathrm{d}\Delta_{\text{mix}}\mathrm{V_m(T)} =\\ &\mathrm{E_{pm}(mix;T)\,dT}\\ &+\left\{\mathrm{V_1(mix;T) - V_1^*(\ell;TMD^*)}\,\left[1+\chi_1\,(\mathrm{T-TMD^*})^2\,[\mathrm{K}]^{-2}\right\}\,\mathrm{dxx_1}\right.\\ &+\left\{\mathrm{V_2(mix;T) - V_2^*(\ell;TMD^*)}\,\left[1+\chi_2\,(\mathrm{T-TMD^*})\,[\mathrm{K}]^{-1}\right]\,\mathrm{dx}\right.\\ &-\mathrm{x_1\,V_1^*(\ell;TMD^*)}\,2\,\chi_1\,(\mathrm{T-TMD^*})\,[\mathrm{K}]^{-2}\right]\,\mathrm{dT}\\ &-\mathrm{x_2\,V_2^*(\ell;TMD^*)}\,\chi_2\,[\mathrm{K}]^{-1}\,\mathrm{dT}\end{aligned}$$

\

We note that $\mathrm{dx_1 = -dx_2}$ and that the coefficients of $\mathrm{dx_1}$ and $\mathrm{dx_2}$ are in fact excess partial molar volumes at temperature T. Hence,

$$\begin{aligned}&\mathrm{d}\Delta_{\text{mix}}\mathrm{V_m(T)} =\\ &\mathrm{E_{pm}(mix;T)\,dT} + \left[\mathrm{V_2^E(T) - V_1^E(T)}\right]\,\mathrm{dxx_2}\\ &\qquad\mathrm{-x_1\,V_1^*(\ell;TMD)}\,2\,\chi_1\,(\mathrm{T-TMD})\,[\mathrm{K}]^{-2}\right]\,\mathrm{dT}\\ &\qquad\mathrm{-\,x_2\,V_2^*(\ell;TMD)}\,\chi_2\,[\mathrm{K}]^{-1}\,\mathrm{dT}\end{aligned}$$

Or,

$$\begin{aligned}\frac{\mathrm{d}\Delta_{\text{mix}}\,\mathrm{V_m(T)}}{\mathrm{dT}} =& \mathrm{E_{pm}(mix;T)} + \left[\mathrm{V_2^E(T) - V_1^E(T)}\right]\,\frac{\mathrm{dx}}{\mathrm{dT}}\\ &\mathrm{-x_1\,V_1^*(\ell;TMD^*)}\,2\,\chi_1\,(\mathrm{T-TMD^*})\,[\mathrm{K}]^{-2}\right]\\ &\mathrm{-\,x_2\,V_2^*(\ell;TMD^*)}\,\chi_2\,[\mathrm{K}]^{-1}\end{aligned}$$

We use equation (n) at temperature '$\mathrm{T}=\theta$' and at fixed composition; i.e. $\mathrm{dx_2}=0$. Moreover, by definition at the TMD, $\mathrm{E_{pm}(mix;\theta)}$ is zero. Hence the dependence of $\Delta_{\text{mix}}\ \mathrm{V_m}(\theta)$ on temperature at fixed pressure and composition is given by equation (o).

$$\begin{aligned}\left(\frac{\partial\Delta_{\text{mix}}\,V_{\mathrm{m}}(\mathrm{T})}{\partial\mathrm{T}}\right)_{\mathrm{p,x(2)}} =& \mathrm{-x_1\,V_1^*(\ell;TMD^*)}\,2\,\chi_1\,(\mathrm{T-TMD^*})\,[\mathrm{K}]^{-2}\right]\\ &\mathrm{-\,x_2\,V_2^*(\ell;TMD^*)}\,\chi_2\,[\mathrm{K}]^{-1}\end{aligned}$$

We identify temperature θ with the recorded TMD. Hence from equation (o) with $\Delta\theta = \theta - \mathrm{TMD^*}$ [4],

$$\Delta\theta = -\frac{\mathrm{x_2\,V_2^*(\ell,TMD^*)}\,\chi_2\,[\mathrm{K}]^{-1}}{2\,(1-\mathrm{x_2})\,\mathrm{V_1^*(\ell,TMD^*)}\,\chi_1\,[\mathrm{K}]^{-2}} - \frac{[\partial\Delta_{\text{mix}}\,\mathrm{V_m}(\theta)/\partial\mathrm{T}]_{\mathrm{p,x(2)}}}{2\,(1-\mathrm{x_2})\,\mathrm{V_1^*(\ell,TMD^*)}\,\chi_1\,[\mathrm{K}]^{-2}}$$

In other words, the shift in the TMD, $\Delta\theta$, is made up of two contributions. For binary system having thermodynamic properties which are ideal, the second term on the r.h.s. of equation (p) is zero. The first term on the r.h.s. side of equation (p) predicts that $\Delta\theta$ is negative in agreement with the Despretz rule. In summary therefore equation (p) can be written in the following simple form.

$$\Delta\theta = \Delta\theta(\text{ ideal }) + \Delta\theta(\text{ struct })$$

The sign of $\Delta\theta(\text{struct})$ is determined by the sign of $[\partial\Delta_{\text{mix}}V_{\text{m}}(\theta)/\partial\text{T}]$. If the latter term is negative, $\Delta\theta(\text{struct})$ is positive and for some systems can be the dominant term. As noted above, this is the case at low mole fractions x_2 for 2-methylpropan-2-ol, a trend attributed to enhancement of water-water hydrogen bonding by the non-aqueous component.

(ii) Aqueous Solutions

The volume of a solution at temperature TMD, prepared using $1\ \text{kg}$ of solvent water and mj moles of a simple neutral solute is given by equation (r).

$$\text{V}(\text{aq};\text{TMD}) = (\text{l}/\text{M}_1)\ \text{V}_1^*(\ell;\text{TMD}) + \text{m}_\text{j}\,\phi\,(\text{V}_\text{j};\text{TMD})$$

But at the TMD,

$$(1/\text{M}_1)\ [\partial\text{V}_1^*(\ell;\text{TMD})/\partial\text{T}] = -\text{m}_\text{j}\ [\partial\phi\,(\text{V}_\text{j};\text{TMD})\,/\partial\text{T}]$$

We use equation (a) to relate $\text{V}_1^*(\ell;\text{TMD})$ to $\text{V}_1^*\,(\ell;\text{TMD}^*)$ with ΔT representing $(\text{TMD} - \ \text{TMD}^*)$.

$$(1/\text{M}_1)\ \text{V}_1^*(\ell;\text{TMD})\,\chi_1\,2\,\Delta\text{T}/[\text{K}]^2 = -\text{m}_\text{j}\ [\partial\phi\,(\text{V}_\text{j};\text{TMD})\,/\partial\text{T}]$$

We assume that for dilute real solutions $\phi\,(\text{V}_j)$ is a linear function of the molality of solute j and that the proportionality term is the pairwise volumetric interaction parameter v_{jj}. Thus,

$$\phi\,(\text{V}_\text{j}) = \phi\,(\text{V}_\text{j})^\infty + \text{v}_\text{jj}\ (\text{m}_\text{j}/\text{m}^0)$$

Then

$$\text{d}\phi\,(\text{V}_\text{j})\,/\text{dT} = \text{d}\phi\,(\text{V}_\text{j})^\infty\,/\text{dT} + [\partial\text{v}_\text{ij}/\partial\text{T}]_\text{p}\ (\text{m}_\text{j}/\text{m}^0)$$

Hence,

$$\left\{2\,\text{V}_1^*\,(\ell;\text{TMD}^*)\ \chi_1/\text{M}_1\,[\text{K}]^2\right\}\ \Delta\text{T} = -\text{m}_\text{j}\ [\partial\phi\,(\text{V}_\text{j}) = \partial\text{T}] - [\partial\text{v}_\text{ij}/\partial\text{T}]\ (\text{m}^0)^{-1}\ (\text{m}_\text{j})^2$$

We rewrite equation (w) as an equation for the change in TMD, ΔT using a quadratic in m_j [5]. Thus,

$$\Delta\text{T} = \text{q}_1\,\text{m}_\text{j} + \text{q}_2\,\text{m}_\text{j}^2$$

Consequently a plot of ΔT m_j is linear having intercept q_1 and slope q_2 [1]. If the solution is ideal [i.e. v_{jj} is zero] then q_2 in zero and $[\Delta\text{T}/\text{m}_\text{j}]$ is constant independent of m_j [6].

(iii) Aqueous Salt Solutions

The above analysis forms the basis for an analysis of the effects of salts on TMD except that the dependence of $\phi\,(\text{V}_j)$ is expressed using the following equation where S_V is the Debye-Huckel Limiting Law volumetric parameter [7-12].

$$\phi\,(V_j) = \phi\,(V_j)^\infty + S_v\ (m_j/m^0)^{1/2} + b\ (m_j/m^0)$$

The foregoing analysis has been extended to include consideration of isobaric expansions [13] and limiting partial molar expansions [14-17].

Footnotes

[1] C. Wada and S.Umeda, Bull. Chem. Soc. Jpn,1962,**35**,646,1797.

[2] F. Franks and B. Watson, Trans. Faraday Soc.,1969,**65**,2339.

[3] The symbol [K] indicates the unit of temperature, kelvin. The term $\left\{1 + \chi_1\ (\text{T} - \text{TMD}^*)^2\,/[\text{K}]^2\right\}$ is dimensionless as required by equation (a).

[4] As noted χ_1 and χ_2 are dimensionless and characteristic properties of the two components.

$$\frac{\mathrm{x}_2\,\mathrm{V}_2^*\,(\ell,\mathrm{TMD}^*)\;\chi_2\,[\mathrm{K}]^{-1}}{2\;(1-\mathrm{x}_2)\;\mathrm{V}_1^*\,(\ell,\mathrm{TMD}^*)\;\chi_1\,[\mathrm{K}]^{-2}}$$
$$= \frac{[1]\;\left[\mathrm{m}^3\;\mathrm{mol}^{-1}\right]\;[1]\,[\mathrm{K}]^{-1}}{[1]\,[1]\;\left[\mathrm{m}^3\;\mathrm{mol}^{-1}\right]\;[1]\,[\mathrm{K}]^{-2}} = [\mathrm{K}]$$
$$\frac{[\partial\Delta_{\mathrm{mix}}\,\mathrm{V}_{\mathrm{m}}(\theta)/\partial\theta]}{2\;(1-\mathrm{x}_2)\;\mathrm{V}_1^*\,(\ell,\mathrm{TMD}^*)\;\chi_1\,[\mathrm{K}]^{-2}} = \frac{\left[\mathrm{m}^3\;\mathrm{mol}^{-1}\;\mathrm{K}^{-1}\right]}{[1]\,[1]\;\left[\mathrm{m}^3\;\mathrm{mol}^{-1}\right]\;[1]\,[\mathrm{K}]^{-2}} = [\mathrm{K}]$$

[5] M. V. Kaulgud, J. Chem. Soc. Faraday Trans.1,1979,**75**,2246; 1990,**86**,911.

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[10] For comments on salts in D2O, see A. J. Darnell and J. Greyson, J. Phys. Chem.,1968, **73**,3032.

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[15] T. M. Herrington and E. L. Mole, J. Chem. Soc. Faraday Trans.1,1982,**78**,213.

[16] D. D. Macdonald and J. B. Hyne, Can. J. Chem.,1976,**54**,3073.

[17] D. D. Macdonald, B. Dolan and J. B. Hyne, J. Solution Chem.,1976,**5**,405.

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1.14.70: Solutions: Neutral Solutes: Inter-Solute Distances

At its simplest a solution comprises one liquid component is vast excess, the solvent, and another, the solute, which is dispersed in the solvent. The solvent is more than just a useful medium in which to disperse the solute although one might argue that a key role is to inhibit associations of the solute molecules. In an even cursory examination of the properties of solutions, a key consideration is the distance between solute molecules. An interesting calculation offers insight into the dependence of solute-solute distances on solute concentration [1]. For a simple non-ionic solute (e.g. urea) in aqueous solution at concentration $\mathrm{c}_j\ \mathrm{moldm}^{-3}$, the average solute-solute distance d is given by equation (a) where $\mathrm{N_A}$ is the Avogadro number.

$$d = (N_A\, c_j)^{-1/3}$$

At $\mathrm{c} = 10^{-2}\ \mathrm{moldm}^{-3}$, $\mathrm{d} = 5.5\ \mathrm{nm}$. If the solute is a 1:1 salt where 1 mole of salt yields two moles of solute ions, $\mathrm{d} = 4.4\ \mathrm{nm}$. With increase in solute concentration, the mean distance between solute molecules decreases.

An interesting feature of aqueous solutions is worthy of comment. If a given water molecule is hydrogen bonded (indicating strong cohesion) to four nearest neighbour water molecules, that water molecule exists in a state of low density-high molar volume. In other words cohesion is linked to low density, a pattern contrary to that encountered in most systems. Nevertheless in reviewing the properties of aqueous solutions and water, one must be wary of overstressing the importance of hydrogen bonding. Indeed liquid water has a modest viscosity which is not the conclusion would draw from some models for liquid water which emphasize the role of water-water hydrogen bonding.

Footnote

[1] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London 2nd. Edn. Revised, 1965.

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1.14.71: Time and Thermodynamics (Timenote)

We note two comments in monographs dealing with thermodynamics.

One comment [1] states that '… thermodynamics deals with systems at equilibrium, time is not a thermodynamic co-ordinate.'

The reference here is in the context of systems at equilibrium [1].

A stronger statement with a different view is made by McGlashan [2].

Thus

> 'We shall be using time t as one of our variables in this chapter. There are those who say that time has no place in thermodynamics. They are wrong.'

Some history sets the scene.

Once upon a time chemists used the calorie as a unit of energy. In fact there were three different units named calorie: thermochemical calorie, international calorie and 150 C calorie. In common they defined energy in terms of the amount of energy required to raise by one Kelvin, the temperature of one gram of pure liquid water under specified conditions of temperature and pressure. Time is not mentioned, directly or indirectly, in this definition. Then Joule showed there is an equivalence between heat and mechanical energy. It is just a small step to relate thermal energy to kinetic energy and, hence, to time. If a calorimetric definition of energy had been adopted, then its unit would be a base unit. In practice, this would be a regression to the situation before Joule determined the mechanical equivalent of heat.

Wood and Battino [1] and McGlashan[2] are both right. Time is an important thermodynamic variable for formulating the conditions under which systems approach an equilibrium state. However, time is not used to describe the properties of these systems after equilibrium is attained.

Footnotes

[1] S. E. Wood and R. Battino, Thermodynamics of Chemical Systems, Cambridge Univeristy Press, Cambridge,1990, page 2.

[2] M. L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979, page 102; the footnotes in this text are often provocative.

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1.14.72: Variables: Independent and Dependent

A colleague has filled a flask with water and asks us by phone to estimate the volume of water in the flask. Clearly this is an impossible task but our colleague offers further information. In answer to the first question, our colleague informs us that there are 2 moles of water in the flask. Immediately we suggest that the volume of water is $36 \mathrm{cm}^3$. Not good enough! Our colleague demands a more precise estimate. We know that the volume of water(ℓ) depends on temperature and pressure and so request new this information. We are told that the temperature is $298.2\ \mathrm{K}$ and the pressure is $101325\ \mathrm{Nm}^{-2}$. We summarize this information in the following form.

$$\mathrm{V} = \mathrm{V}\left[298.2\ \mathrm{K}; 101325\ \mathrm{N\ m\ m}^{-2}; (\ell); 2\ \mathrm{moles}\ \right]$$

Our colleague offers further information such as the vapor pressure and heat capacity of water(ℓ) under these conditions. But we decline this offer on the grounds that no further information is required. We know that having defined the variables in the square brackets [.....], a unique volume V is defined. We may not immediately know the actual volume but given a little time in a scientific library we will be in a position to report volume V.

The variables in the square brackets are the INDEPENDENT VARIABLES [1]. For a system containing one chemical substance we define the volume as follows.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1\right]$$

The term independent means that within limits [1] we can change T independently of the pressure and n_1; change p independently of T and n_1; change n_1 independently of T and p. There are some restrictions in our choice of independent variables. At least one variable must define the amount of all chemical substances in the system and one variable must define the 'hotness' of the system.

The molar volume of liquid chemical substance 1 at the specified temperature and pressure, $V_1^*(\ell)$ is obtained from equation (b) by fixing n_1 at 1 mol. Thus

$$\mathrm{V}_1^*(\ell) = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1 = 1\ \mathrm{mol}\right]$$

If the composition of a given closed system is specified in terms of the amounts of two chemical substances, 1 and 2, four independent variables $[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2]$ define the independent variable V [2]. Thus

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2\right]$$

Actually there is merit in writing equation (d) in terms of three intensive variables which in turn defines the molar volume V_m of the binary system at given mole fraction $x_1 = 1 - x_2$. Thus

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{x}_1\right]$$

For a system containing i - chemical substances where the amounts can be independently varied, the dependent extensive variable V is defined by equation (f).

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_2 \ldots \ldots \ldots, \mathrm{n}_\mathrm{i}\right]$$

Similarly the dependent intensive variable V_m is defined by equation (g).

$$\mathrm{V}_\mathrm{m} = \mathrm{V}_\mathrm{m}\left[\mathrm{T}, \mathrm{p}, \mathrm{x}_1, \mathrm{x}_2 \ldots \ldots \ldots, \mathrm{x}_{\mathrm{i}-1}\right]$$

Footnotes

[1] The phrase 'independent variable' is important. With reference to the properties of an aqueous solution containing ethanoic acid, the number of components for such a solution is 2, amount of water and amount of ethanoic acid. The actual amounts of ethanoic acid, water, ethanoate and hydrogen ions are determined by an equilibrium constant which is an intrinsic property of this system at given T and p. From the point of the Phase Rule [2], the number of components equals 2. For the same reason when we consider the volume of a system containing only n_j moles of water we disregard evidence that water partly self-dissociates into $\mathrm{H}^+(\mathrm{aq})$ and $\mathrm{OH}^-(\mathrm{aq})$.

[2] In terms of the Phase Rule, for two components ($\mathrm{C} = 2$) and one phase ($\mathrm{P} = 1$), the number of degrees of freedom F equals 3. These degrees of freedom refer to a set of intensive variables. Hence, for a solution where substance 1 is the solvent and substance

2 is the solute, the system is defined by specifying the three (intensive) degrees of freedom, T, p and, for example, solute molality.

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1.14.73: Variables: Gibbsian and Non-Gibbsian

Experience shows that the thermodynamic state of a closed single phase system can be defined by a minimum set of independent variables where at least one variable is a measure of the 'hotness' of the system; e.g. temperature. The volume of an aqueous solution containing n_1 moles of water and n_j moles of urea is defined by the set of independent variables, $\mathrm{T},\ \mathrm{p},\ \mathrm{n}_1$ and n_j.

$$\mathrm{V} = \mathrm{V}\left[\mathrm{T}, \mathrm{p}, \mathrm{n}_1, \mathrm{n}_\mathrm{j}\right]$$

Having defined the parameters set out in the brackets [...] the volume of the system, the dependent variable, is uniquely defined. In fact we can replace V in this equation by $\mathrm{G},\ \mathrm{H}$ and S in order to define unique Gibbs energy, enthalpy and entropy respectively.

The set of independent variables in equation (a) is called Gibbsian because the set comprises the intensive variables T and p together with the extensive composition variables [1]. The general form of equation (a) defining the thermodynamic potential function, Gibbs energy G is as follows where ξ is the extensive composition variable.

$$\mathrm{G} = \mathrm{G}[\mathrm{T}, \mathrm{p}, \xi]$$

Other sets of independent variables are used in conjunction of the thermodynamic potential functions, enthalpy H, energy U and Helmholtz energy F.

$$\mathrm{F} = \mathrm{F}[\mathrm{T}, \mathrm{V}, \xi]$$

$$\mathrm{U} = \mathrm{U}[\mathrm{S}, \mathrm{V}, \xi]$$

$$\mathrm{H} = \mathrm{H}[\mathrm{S}, \mathrm{p}, \xi]$$

In equations (c) and (d), V is an extensive variable and in equations (d) and (e) S is an extensive variable. The sets of independent variables in equations (c), (d) and (e) are called non-Gibbsian [1].

Footnote

[1] J. C. R. Reis, M. J. Blandamer, M. I. Davis and G. Douhéret, Phys. Chem. Chem. Phys., 2001, **3**, 1465.

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1.14.74: Vaporization

A given chemical substance j can exist in phases I and II. For phase I,

$$\mathrm{U_j^*(I) = H_j^*(I) - p\,V_j^*(I)} \tag{1.14.74.1}$$

$\mathrm{U_j^*(I),\ H_j^*(I)\ and\ V_j^*(I)}$ are the molar thermodynamic energy, enthalpy and volume respectively of chemical substance j in phase I at pressure p. Chemical substance j can also exist in phase II at the same pressure p.

$$\mathrm{U_j^*(II) = H_j^*(II) - p\,V_j^*(II)} \tag{1.14.74.2}$$

Equations 1.14.74.1 and 1.14.74.2 are quite general. In an important application we identify phase II as the vapor phase which we assume to have the properties of a perfect gas. Phase I is the liquid state. For the process `liquid → vapor' (i.e. vaporization) at temperature T,

$$\mathrm{\Delta_{vap}\,U_j^*(\,T) = \Delta_{vap}H_j^*(\,T) - p\,\left[V_j^*(\,g) - V_j^*(\ell)\right]}$$

But at temperature T, $\mathrm{V_j^*(\,g) - V_j^*(\ell) \gg 0}$ Also for one mole of a perfect gas, $\mathrm{p\,V_j^*(\,g) = R\,T}$.

Hence,

$$\mathrm{\Delta_{vap}\,U_j^*(\,T) = \Delta_{vap}\,H_j^*(\,T) - R\,T}$$

$\mathrm{\Delta_{vap}\,H_j^N(T)}$ is obtained from the dependence of vapour pressure on temperature; see Clausius - Clapeyron Equation. Hence we obtain the molar thermodynamic energy of vaporisation.

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1.14.75: Viscosities: Salt Solutions

The (shear) viscosities of salt solutions have been extensively studied [1,2]. A frequently cited paper (always worth reading in terms of the care taken in the experimental study) was published by Jones and Dole [3]. The dependence of the viscosity of an aqueous salt solution $\eta(\mathrm{aq})$ (at fixed temperature and pressure) on concentration of salt j is described by the **Jones-Dole equation**; equation (a) where $\eta_1^*(\ell)$ is the viscosity of water(ℓ) at the same T and p [3,4].

$$\eta(\mathrm{aq})/\eta_1^*(\ell) = 1 + \mathrm{A}\,\mathrm{c_j}^{1/2} + \mathrm{B}\,\mathrm{c_j}$$

Equation (a) is re-expressed as follows. By definition;

$$\psi = [\eta(\mathrm{aq}) - \eta_1^*(\ell)] \,/\, \left[\eta_1^*(\ell)\,\mathrm{c_j}^{1/2}\right]$$

Hence

$$\psi = \mathrm{A} + \mathrm{B}\,\mathrm{c_j}^{1/2}$$

A plot of ψ against $(\mathrm{c_j})^{1/2}$ has intercept A and slope B, the Jones-Dole B-viscosity coefficient [5]. The A coefficient describes the impact of charge-charge interactions on the viscosity of a solution, being generally positive and estimated using the Falkenhagen equation [6-8]. The B coefficient characterizes ion-solvent interactions at defined T and p. For a 1:1 salt j, the B_j coefficient for salt j is expressed as the sum of ionic B coefficients.

$$\mathrm{B_j} = \mathrm{B_+} + \mathrm{B}$$

For example, B_j for a series of salts with a common anion, the changes in B_j reflect changes in B_+ for the cations. The pattern in $\mathrm{B}\,(\mathrm{R_4N^+\ I^-; aq; 298.2\ K})$ reflects the changes in $\mathrm{B}\,(\mathrm{R_4N^+\ I^-; aq; 298.2\ K})$ through the series from R = methyl to R = n-butyl. In fact the change in this case is indicative of the change in character from 'structure breaking' $\mathrm{Me_4N^+}$ to hydrophobic 'structure forming' $\mathrm{Bu_4N^+}$ ions [9]. In broad terms a positive B coefficient indicates a tendency for the solute to enhance water-water interactions and thus raise the viscosity whereas a negative coefficient indicates a tendency to induce disorder [10]. Ionic B-viscosity coefficients are linked to the hydration properties of ions. An important link was suggested by Gurney [11]. On the grounds that $\mathrm{K^+}$ and $\mathrm{Cl^-}$ ions are roughly the same size, Gurney argued that for aqueous solutions, $\mathrm{B}\,(\mathrm{K^+}) = \mathrm{B}\,(\mathrm{Cl^-})$. Hence one can estimate single-ion B-viscosity coefficients. A negative B-ionic coefficient indicates that the ion is a 'structure breaker' and a positive B-ionic viscosity coefficient indicates that the ion is a 'structure former'.

The terms 'structure breaker' and 'structure former' were extensively used in the decades from 1950 to 1990. However their popularity waned towards the end of the century as more precise descriptions of ionic hydration were sought.

Footnotes

[1] We confine attention to shear viscosities (i.e. resistance to shear). The related bulk viscosities (i.e. resistance to compression) are rarely discussed in the present context.

[2] Units; dynamic viscosity; traditional unit = poise, symbol P

$\mathrm{P} = 10^{-1}\ \mathrm{Pas}$. But $\mathrm{Pa} = \ \mathrm{kgm^{-1}\ s^{-2}}$ Then \(\mathrm{P} = 10^{-1} \mathrm{~kg m}^{-1} \mathrm{~s}^{-1} SI unit; η = [kg m-1 s-1]

[3] G. Jones and M. Dole, J. Am. Chem. Soc., 1929,**51**,2950.

[4] Other equations have been suggested as alternatives to the Jones-Dole equation.

a. The concentration cj is replaced by the ionic strength of the salt solution; C. Wu, J. Phys Chem.,1968,**72**,2663.
b. For non-electrolytes, the coefficient A is zero but a new term is usually added linear in the concentration of solute.
    i. R. Robinson and R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon, London, 1965.
    ii. W. Devine and B. M. Lowe, J.Chem.Soc.,A,1971,2113.
c. The ratio $\eta(\mathrm{aq})/\eta_1^*(\ell)$ is expressed as a function of the volume fraction of the solute.
    i. D. G. Thomas, J. Colloid. Interface Sci.,1965,**20**,267.

ii. B. R. Breslau and I. F. Mikker, J. Phys. Chem.,1970,**74**,1056.
iii. J. Vand, J.Phys.Chem.,1948,**52**,277.
iv. D. Eagland and G. Pilling, J. Phys. Chem., 1 972,**76**,1902.

d. Add a term linear in $(c_j)^2$ to equation (a). N. Martinus, C. D. Sinclair and C. A. Vincent, Electrochim. Acta, 1977,**22**,1183.
e. Somewhat outside the terms of reference of the account developed here is a treatment of viscosity in terms of kinetic phenomena; e.g. in terms of Transition State Theory. S. Glasstone, K. J. Laidler and H. Eyring, Theory of Rate Processes, McGraw-Hill, New York,1941. For application of this model see for example,

i. W. Good, Electrochim. Acta, 1964, **9**, 203; 1965, **10**,1; 1966, **11**, 759,767; 1967, **12**,103 1.
ii. J. C. MacDonald, Electrochim. Acta, 1972,**17**,1965.

[5] See for example,

i. R. L. Kay, K. T. Vituccio, C. Zawoyski and D. F. Evans. J. Phys. Chem.,1966, **70**, 2336.
ii. Y. Tamaki, Y. Ohara, M. Inabe, T. Mori and F. Numata, Bull. Chem. Soc. Jpn.,1983,**56**,1930.

[6] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold, New York, 3rd. edition, 1958,p.240.

[7] See for example;

a. A. Kacperska, S. Taniewska-Osinska, A. Bald and S. Szejgis, J. Chem. Soc. Faraday Trans.1,1989,**85**,4147.
b. A. Sacco, G. Petrella, A. Dell'Atti and A. de Giglio, J. Chem. Soc. Faraday Trans.1, 1982,**78**,1507.

[8] An alternative approach involves calculating the A coefficient using the Falkenhagen theory and hence writing the Jones-Dole equation as follows.

$$\eta(\mathrm{aq})/\eta_{\mathrm{I}}^{*}(\ell) - 1 - \mathrm{A}\ (\mathrm{c_j})^{1/2} = \mathrm{B}\,\mathrm{c_j}$$

In a plot of the LHS of this equation against c_j, the slope equals B. See for example, K. Tamaki, K. Suga and E. Tanihara, Bull. Chem. Soc. Jpn.,1987.**60**,1225.

[9] B. M. Lowe and G. A. Rubienski, Electrochem. Acta, 1974,**19**,393.

[10] E. R. Nightingale, J. Phys. Chem.,1959,**63**,1381;1962,**66**,894. See also, D. T. Burns, Electrochim Acta, 1965,**10**,985.

[11] R. W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.

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1.14.76: Work

This term ‘work’ makes it first key appearance (at least in thermodynamics) in the context of the statement that if work is done on a closed system the thermodynamic energy of the system increases given that heat q is zero. This simple statement understates the complexity of the term ‘work’ in thermodynamics.

In general terms work done on a closed thermally insulated system raises the energy of that system and is given by the product of intensive and capacity factors [1]. Three examples make the point.

a.
b.
c.

The analysis is complicated by the fact that changes in a given system can take one of two limiting forms; e.g. frozen and equilibrium. In the case of surface tension, frozen (plastic) surface tension describes the case where the intermolecular distances in the surface increase. The equilibrium case describes the case where molecules in the bulk phase and in the surface exchange to hold the change in the surface as a reversible (equilibrium) process.

Footnote

[1] E. F. Caldin, Chemical Thermodynamics, Clarendon Press, Oxford, 1958.

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