CHEM 342: PHYSICAL CHEMISTRY II



Kathryn Davis
Manchester University

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CHEM 342: Physical Chemistry II

Kathryn Davis

Manchester University

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Licensing

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CHAPTER OVERVIEW

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1.1: Overview of Classical Thermodynamics

One of the pioneers in the field of modern thermodynamics was James P. Joule (1818 - 1889). Among the experiments Joule carried out, was an attempt to measure the effect on the temperature of a sample of water that was caused by doing work on the water. Using a clever apparatus to perform work on water by using a falling weight to turn paddles within an insulated canister filled with water, Joule was able to measure a temperature increase in the water.

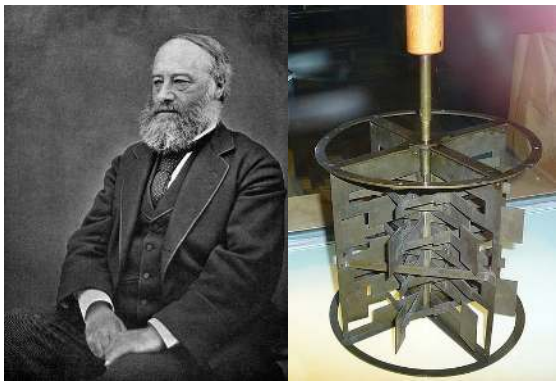


Figure **1.1.1**: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

Thus, Joule was able to show that work and heat can have the same effect on matter – a change in temperature! It would then be reasonable to conclude that heating, as well as doing work on a system will increase its energy content, and thus it's ability to perform work in the surroundings. This leads to an important construct of the **First Law of Thermodynamics**:

> *The capacity of a system to do work is increased by heating the system or doing work on it.*

The **internal energy** (U) of a system is a measure of its capacity to supply energy that can do work within the surroundings, making U the ideal variable to keep track of the flow of heat and work energy into and out of a system. Changes in the internal energy of a system (ΔU) can be calculated by

$$\Delta U = U_f - U_i \tag{1.1.1}$$

where the subscripts i and f indicate initial and final states of the system. U as it turns out, is a state variable. In other words, the amount of energy available in a system to be supplied to the surroundings is independent on how that energy came to be available. That's important because the manner in which energy is transferred is path dependent.

There are two main methods energy can be transferred to or from a system. These are suggested in the previous statement of the first law of thermodynamics. Mathematically, we can restate the first law as

$$\Delta U = q + w$$

or

$$dU = dq + dw$$

where q is defined as the amount of energy that flows into a system in the form of **heat** and w is the amount of energy lost due to the system doing **work** on the surroundings.

Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system ($q_{system} > 0$, $q_{surroundings} < 0$). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** ($q_{system} < 0$, $q_{surroundings} > 0$). In the absence of any energy flow in the form or work, the flow of heat into or out of a system can be measured by a change in temperature. In cases where it is difficult to measure temperature changes of the system directly, the amount of heat energy

transferred in a process can be measured using a change in temperature of the soundings. (This concept will be used later in the discussion of calorimetry).

An infinitesimal amount of heat flow into or out of a system can be related to a change in temperature by

$$dq = C\,dT$$

where C is the **heat capacity** and has the definition

$$C = \frac{dq}{\partial T}$$

Heat capacities generally have units of (J mol^{-1} K^{-1}) and magnitudes equal to the number of J needed to raise the temperature of 1 mol of substance by 1 K. Similar to a heat capacity is a **specific heat** which is defined per unit mass rather than per mol. The specific heat of water, for example, has a value of 4.184 J g^{-1} K^{-1} (at constant pressure – a pathway distinction that will be discussed later.)

Example 1.1.1: Heat required to Raise Temperature

How much energy is needed to raise the temperature of 5.0 g of water from 21.0 °C to 25.0 °C?

Solution

$$\begin{aligned} q &= mC\Delta T \\ &= (5.0\ \cancel{g})(4.184\frac{J}{\cancel{g}\ \cancel{^\circ C}})(25.0\cancel{^\circ C} - 21.0\cancel{^\circ C}) \\ &= 84\,J \end{aligned}$$

What is a partial derivative?

A partial derivative, like a total derivative, is a slope. It gives a magnitude as to how quickly a function changes value when one of the dependent variables changes. Mathematically, a partial derivative is defined for a function $f(x_1, x_2, \ldots x_n)$ by

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i} = \lim_{\Delta_i \to 0}\left(\frac{f(x_1 + \Delta x_1, x_2 + \Delta x_2, \ldots, x_i + \Delta x_i, \ldots x_n + \Delta x_n) - f(x_1, x_2, \ldots x_i, \ldots x_n)}{\Delta x_i}\right)$$

Because it measures how much a function changes for a change in a given dependent variable, infinitesimal changes in the in the function can be described by

$$df = \sum_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i}$$

So that each contribution to the total change in the function f can be considered separately.

For simplicity, consider an ideal gas. The pressure can be calculated for the gas using the ideal gas law. In this expression, pressure is a function of temperature and molar volume.

$$p(V,T) = \frac{RT}{V}$$

The partial derivatives of p can be expressed in terms of T and V as well.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{1.1.2}$$

and

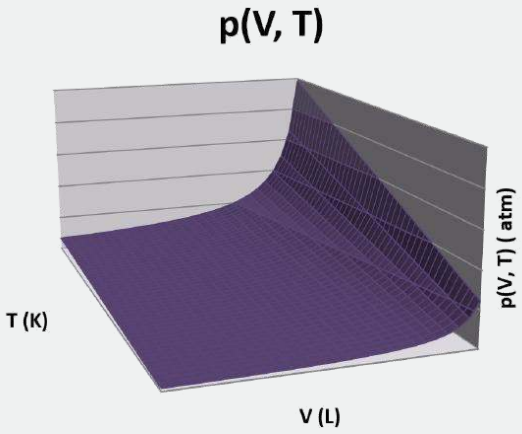
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{1.1.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{1.1.4}$$

or by substituting Equations 1.1.2 and 1.1.3

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT$$



Macroscopic changes can be expressed by integrating the individual pieces of Equation 1.1.4 over appropriate intervals.

$$\Delta p = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial p}{\partial T}\right)_V dT$$

This can be thought of as two consecutive changes. The first is an **isothermal** (constant temperature) expansion from V_1 to V_2 at T_1 and the second is an **isochoric** (constant volume) temperature change from T_1 to T_2 at V_2. For example, suppose one needs to calculate the change in pressure for an ideal gas expanding from 1.0 L/mol at 200 K to 3.0 L/mol at 400 K. The set up might look as follows.

$$\Delta p = \underbrace{\int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV}_{\text{isothermal expansion}} + \underbrace{\int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT}_{\text{isochoric heating}}$$

or

$$\begin{aligned}
\Delta p &= \int_{1.0\ L/mol}^{3.0\ L/mol} \left(-\frac{R(400\ K)}{V^2}\right) dV + \int_{200\ K}^{400,\ K} \left(\frac{R}{1.0\ L/mol}\right) dT \\
&= \left[\frac{R(200\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} + \left[\frac{RT}{3.0\ L/mol}\right]_{200\ K}^{400\ K} \\
&= R\left[\left(\frac{200\ K}{3.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{200\ K}{3.0\ L/mol}\right)\right] \\
&= -5.47\ atm
\end{aligned}$$

Alternatively, one could calculate the change as an isochoric temperature change from T_1 to T_2 at V_1 followed by an isothermal expansion from V_1 to V_2 at T_2:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT + \int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV$$

or

$$\begin{aligned}\Delta p &= \int_{200\ K}^{400,\ K}\left(\frac{R}{1.0\ L/mol}\right)dT + \int_{1.0\ L/mol}^{3.0\ L/mol}\left(-\frac{R(400\ K)}{V^2}\right)dV \\ &= \left[\frac{RT}{1.0\ L/mol}\right]_{200\ K}^{400\ K} + \left[\frac{R(400\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} \\ &= R\left[\left(\frac{400\ K}{1.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{400\ K}{1.0\ L/mol}\right)\right] \\ &= -5.47\ atm\end{aligned}$$

This results demonstrates an important property of pressure in that pressure is a state variable, and so the calculation of changes in pressure do not depend on the pathway!

Work

Work can take several forms, such as expansion against a resisting pressure, extending length against a resisting tension (like stretching a rubber band), stretching a surface against a surface tension (like stretching a balloon as it inflates) or pushing electrons through a circuit against a resistance. The key to defining the work that flows in a process is to start with an infinitesimal amount of work defined by what is changing in the system.

Table 3.1.1: Changes to the System

Type of work	Displacement	Resistance	dw
Expansion	dV (volume)	-p_{ext} (pressure)	-p_{ext}dV
Electrical	dQ (charge)	W (resistence)	-W dQ
Extension	dL (length)	-t (tension)	t dL
Stretching	dA	-s (surf. tens.)	sdA

The pattern followed is always an infinitesimal displacement multiplied by a resisting force. The total work can then be determined by integrating along the pathway the change follows.

✔ Example 1.1.2: Work from a Gas Expansion

What is the work done by 1.00 mol an ideal gas expanding from a volume of 22.4 L to a volume of 44.8 L against a constant external pressure of 0.500 atm?

Solution

$$dw = -p_{ext}dV$$

since the pressure is constant, we can integrate easily to get total work

$$\begin{aligned}w &= -p_{exp}\int_{V_1}^{V_2} dV \\ &= -p_{exp}(V_2 - V_1) \\ &= -(0.500\ am)(44.8\ L - 22.4\ L)\left(\frac{8.314\ J}{0.08206\ atm\ L}\right) \\ &= -1130\ J = -1.14\ kJ\end{aligned}$$

Note: The ratio of gas law constants can be used to convert between atm·L and J quite conveniently!

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1.2: Pressure-Volume Work

Work in general is defined as a product of a force $\mathbf{F}$ and a path element $\mathbf{ds}$. Both are vectors and work is computed by integrating over their inner product:

$$w = \int \mathbf{F} \cdot \mathbf{ds}$$

Moving an object against the force of friction as done in the above dissipation experiment is but one example of work:

$$w_{friction} = \int \mathbf{F}_{\text{friction}} \cdot \mathbf{ds}$$

We could also think of *electrical* work. In that case we would be moving a charge e (e.g. the negative charge of an electron) against an electrical (vector) field $\mathbf{E}$. The work would be:

$$w_{electical} = \int e\mathbf{E} \cdot \mathbf{ds}$$

Other examples are the stretching of a rubber band against the elastic force or moving a magnet in a magnetic field etc, etc.

Pressure-volume (PV) work

In the case of a cylinder with a piston, the pressure of gas molecules on the inside of the cylinder, P, and the gas molecules external to the piston, P_{ext} both exert a force against each other. Pressure, (\P\), is the force, F, being exerted by the particles per area, A:

$$P = \frac{F}{A}$$

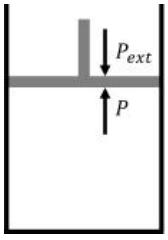


Figure 19.2.1 : A piston with internal pressure P and external pressure P_{ext}.

We can assume that all the forces generated by the pressure of the particles operate parallel to the direction of motion of the piston. That is, the force moves the piston up or down as the movement of the piston is constrained to one direction. The piston moves as the molecules of the gas rapidly equilibrate to the applied pressure such that the internal and external pressures are the same. The result of this motion is work:

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\,ds) = \int P\,dV \tag{1.2.1}$$

This particular form of work is called **pressure-volume (PV) work** and will play an important role in the development of our theory. Notice however that volume work is only ***one form*** of work.

Sign Conventions

It is important to create a sign convention at this point: positive heat, positive work is always energy you put in into the system. If the system decides to remove energy by giving off heat or work, that gets a minus sign.

In other words: ***you pay the bill***.

To comply with this convention we need to rewrite volume work (Equation 1.2.1) as

$$w_{PV} = -\int \left(\frac{F}{A}\right)(A\,ds) = -\int P\,dV$$

> Hence, to decrease the volume of the gas (ΔV is negative), we must put in (positive) work.

Thermodynamics would not have come very far without cylinders to hold gases, in particular steam. The following figure shows when the external pressure, P_{ext}, is greater than and less than the internal pressure, P, of the piston.

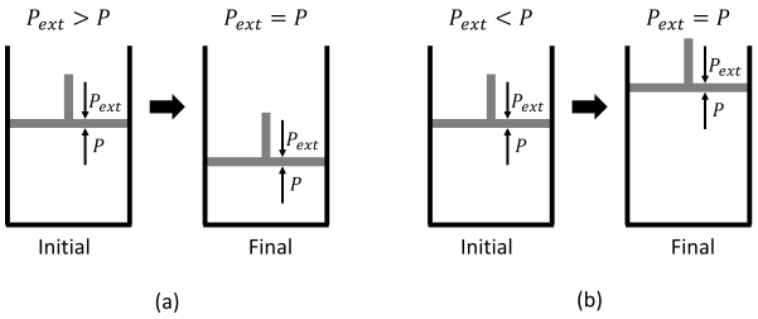


Figure 19.2.2 : Pistons showing a compression (left) and an expansion (right).

If the pressure, P_{ext}, being exerted on the system is constant, then the integral becomes:

$$w = -P_{ext} \int_{V_{initial}}^{V_{final}} dV = -P_{ext} \Delta V \tag{1.2.2}$$

Since the system pressure (inside the piston) is not the same as the pressure exerted on the system, the system is not in a state of equilibrium and cannot be shown directly on and PV diagram. This type of process is called an irreversible process. For a system that undergoes irreversible work at constant external pressure, we can show the amount of work being done on a PV diagram despite not being able to show the process itself.

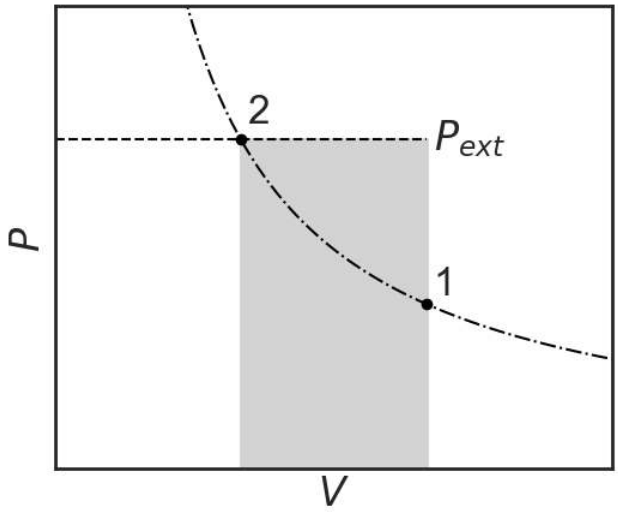


Figure 19.2.3 : A system is compressed under constant external pressure, P_{ext}, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible compression are the same.

Note that the external pressure, P_{ext}, exerted on the system is constant. If the external pressure changes during the compression, we must *integrate* over the whole range:

$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}(V)\, dV$$

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1.3: Work and Heat are not State Functions

Heat and work are path functions

Heat (q) and work (w) are path functions, not state functions:

1. They are path dependent.
2. They are energy transfer → they are not intrinsic to the system.

Path Functons

Functions that depend on the path taken, such as work (w) and heat (q), are referred to as **path functions**.

Reversible versus irreversible

Let's consider a piston that is being compressed at constant temperature (isothermal) to half of its initial volume:

1. Start with cylinder 1 liter, both external and internal pressure 1 bar.
2. ***Peg*** the piston in a fixed position.
3. Put cylinder in a pressure chamber with $P_{ext} = 2$ bar.
4. Suddenly pull the peg.

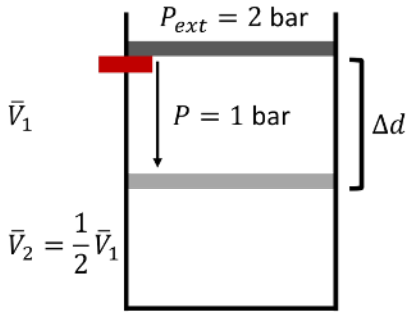


Figure 19.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

The piston will shoot down till the internal and external pressures balance out again and the volume is 1/2 L. Notice that the external pressure was ***maintained*** constant at 2 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time. In a $P-V$ diagram of an ideal gas, P is a hyperbolic function of V under constant temperature (isothermal), but this refers to the *internal* pressure of the gas. It is the external one that counts when computing work and they are not necessarily the same. As long as $P_{external}$ is constant, work is represented by a rectangle.

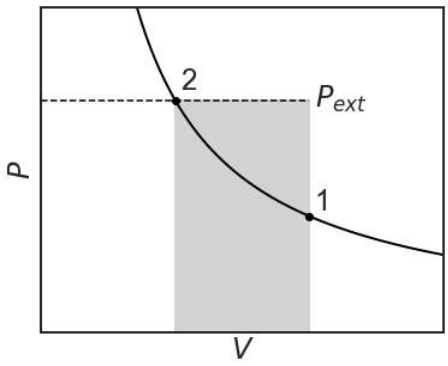


Figure 19.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

The amount of work being done is equal to the shaded region and in equation:

$$w = -\int_{V_1}^{V_2} PdV = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the maximum amount of work that can be done for an isothermal compression. Work is being done on the system, so the overall work being done is positive. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

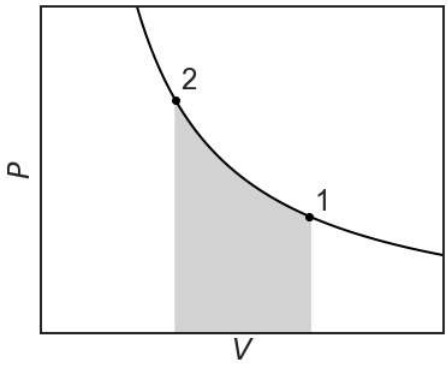


Figure 19.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

For an ideal gas, the amount of work being done along the reversible compression is:

$$w = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2} \frac{1}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

The amount of work being done to the two systems are not the same in the two diagrams (see the gray areas). Work is not a state, but a path function, as it depends on the path taken. You may say, what's the big difference. In both cases, the system is compressed from state 1 to state 2. The key is the word ***suddenly***. By pegging the position in place for the first compression, we have created a situation where the external pressure is higher than the internal pressure ($P_{ext} > P$). Because work is done suddenly by pulling the peg out, the internal pressure is struggling to catch up with the external one. During the second compression, we have $P_{ext} = P$ at all times. It's a bit like falling off a cliff versus gently sliding down a hill. Path one is called an irreversible path, the second a reversible path.

Reversible vs. Irreversible Processes

A reversible path is a path that follows a series of states at rest (i.e., the forces are allowed to balance at all times). In an irreversible one the forces only balance at the very end of the process.

Notice that less work is being done on the reversible isothermal compression than the one-step irreversible isothermal compression. In fact, the minimum amount of work that can be done during a compression always occurs along the reversible path.

Isothermal Expansion

Let's consider a piston that is being expanded at constant temperature (isothermal) to twice of its initial volume:

1. Start with cylinder 1 liter in a pressure chamber with both an external and internal pressure of 2 bar.
2. ***Peg*** the piston in a fixed position.
3. Take the cylinder out of the pressure chamber with P_{ext}= 1 bar.
4. Suddenly pull the peg.

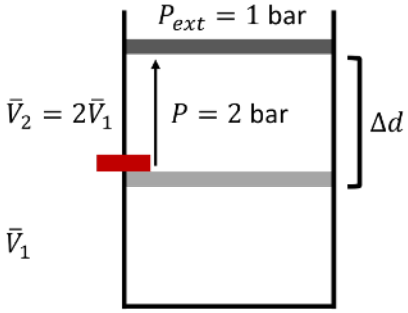


Figure 19.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

The piston will shoot up till the internal and external pressures balance out again and the volume is 2 L. Notice that the external pressure was ***maintained*** constant at 1 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time.

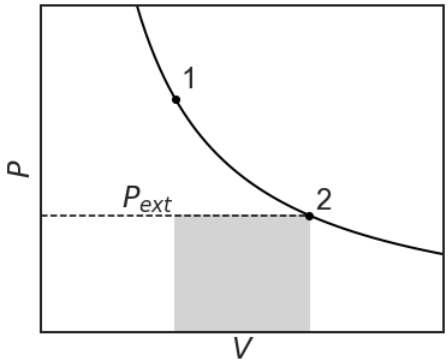


Figure 19.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

The amount of irreversible work being done is again equal to the shaded region and the equation:

$$w = -P\Delta V = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the minimum amount of work that can be done for an isothermal expansion. Work is being done on the system, so the overall work being done is negative. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

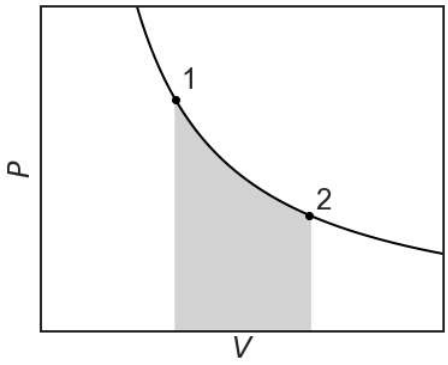


Figure 19.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

Notice that not only is more work is being done than the one-step irreversible isothermal expansion, but it is the same amount of work being done as the reversible isothermal compression. This is the maximum amount of work that can be done during an expansion.

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1.4: Energy is a State Function

Work and heat are not state functions

A Better Definition of the First law of thermodynamics

The change in internal energy of a system is the sum of w and q, which is a state function.

The realization that work and heat are both forms of energy transfer undergoes quite an extension by saying that internal energy is a state function. It means that although heat and work can be produced and destroyed (and transformed into each other), energy is conserved. This allows us to do some serious bookkeeping! We can write the law as:

$$\Delta U = w + q$$

But the (important!) bit about the state function is better represented if we talk about small changes of the energy:

$$dU = \delta w + \delta q$$

We write a straight Latin d for U to indicate when the change in a state function, where as the changes in work and heat are path-dependent. This is indicated by the 'crooked' δ. We can represent changes as integrals, but only for U can we say that regardless of path we get $\Delta U = U_2 - U_1$ if we go from state one to state two. (I.e. it only depends on the end points, not the path).

Notice that when we write dU or δq, we always mean infinitesimally small changes, i.e. we are implicitly taking a limit for the change approaching zero. To arrive at a macroscopic difference like ΔU or a macroscopic (finite) amount of heat q or work w **we need to integrate**.

We will now invoke the **first law of thermodynamics**:

- $dU = \delta q + \delta w$
- $\oint dU = 0$
- Internal energy is conserved

These are all ways of saying that internal energy is a state function.

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1.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred

Isothermal expansion of an ideal gas

For a monatomic ideal gas we have seen that energy $\langle E \rangle$ observed as $U = 3/2nRT$. This means that energy is only dependent on temperature and if a gas is compressed **isothermally**, then the internal energy does not change:

$$\Delta U_{isothermal-idealgas} = 0$$

This means that the reversible work must ***cancel*** the reversible heat:

$$\Delta U_{rev} = w_{rev} + q_{rev} = 0$$

Therefore

$$w_{rev} = -q_{rev}$$

so from the expression of the reversible work for expansion in the last section

$$q_{rev} = nRT \ln \frac{V_2}{V_1}$$

If $V_2 > V_1$ (expansion), then you (or the environment) **must** put heat into the system because this is a positive number.

Adiabatic expansion of an ideal gas

Now suppose you make sure that no heat can enter the cylinder. (Put it in styrofoam or so). Then the path can still be reversible (slow pulling) but the process is then adiabatic.

> *This bat- part comes from a Greek verb βαινω (baino) that means walking, compare acro**bat**, someone who goes high places (acro-). The δια (dia) part means 'through' (cf. diagram, diorama, diagonal etc.) and the prefix α- (a-) denies it all (compare atypical versus typical).*

So the styrofoam prevents the heat from walking through the wall. When expanding the gas from V_1 to V_2 it still does reversible work but where does that come from? It can only come from the internal energy itself. So in this case any energy change should consist of work (adiabatic means: $\delta q = 0$).

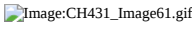
$$dU = \delta w_{rev}$$

This implies that the temperature must drop, because if U changes, then T must change.

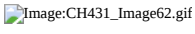
The change of energy with temperature at constant volume is known as the heat capacity (at constant volume) C_v

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

For an ideal gas U only changes with temperature, so that



or:



We can now compare two paths to go from state P_1, V_1, T_1 to state P_2, V_2, T_1:

1. Reversible isothermal expansion A
2. Reversible adiabatic expansion B followed by reversible isochoric heating C

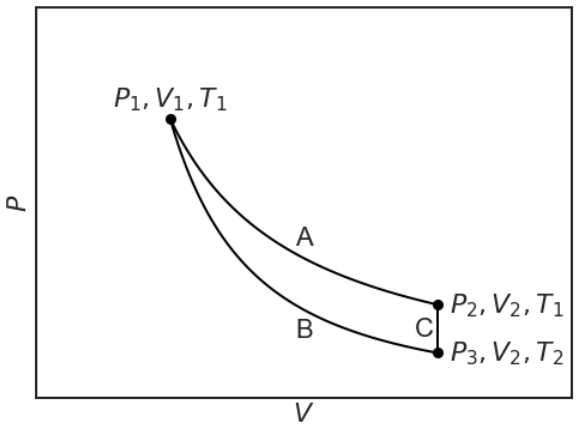


Figure __:

Notice that the temperature remains T_1 for path A (isotherm!), but that it drops to T_2 on the adiabat B, so that the cylinder has to be isochorically warmed up, C, to regain the same temperature.

ΔU_{tot} should be the same for both path A and the combined path B+C, because the end points are the same (U is a state function!). As the and points are at the same temperature and U only depends on T:

$$\Delta U_{tot} = 0$$

Along adiabat B:

$$q_{rev} = 0$$

Along isochoric heating C, there is no volume work because the volume is kept constant, so that:

Image:CH431_Image63.gif

This is the only reversible heat involved in path B+C. However, we know that ΔU_{tot} for path A is zero (isothermal!). This means that the volume work along B must cancel the heat along C:

The book keeping looks as follows, all paths are reversible:

$$\Delta U_{B+C} = \Delta U_A = 0 = q_B + w_B + q_C + w_C$$

We know that $q_B = 0$ since it is an adiabat and $w_C = 0$ since it is an isochore:

$$\Delta U_{B+C} = \Delta U_A = 0 = 0 + w_B + q_C + 0$$

Therefore:

$$w_B = -q_C$$

We had already seen before that along the isotherm A:

$$w_A = -q_A = -nRT \ln \frac{V_1}{V_2}$$

As you can see \w_A\) and w_B are ***not*** the same. Work is a path function, even if reversible. As we are working with an ideal gas we can be more precise about w_B and q_c as well. The term w_B along the adiabat is reversible volume work. Since there is no heat along B we can write a straight d instead of δ for the work contributions (It is the only contribution and must be identical to the state function dU):

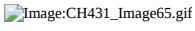
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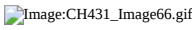
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1.6: The Temperature of a Gas Decreases in a Reversible Adiabatic Expansion

We can make the same argument for the heat along C. If we do the three processes A and B+C only to a tiny extent we can write:



And now we can integrate from V_1 to V_2 over the reversible adiabatic work along B and from T_1 to T_2 for the reversible isochoric heat along C. To separate the variables we do need to bring the temperature to the right side of the equation.:



The latter expression is valid for a reversible adiabatic expansion of a monatomic ideal gas (say Argon) because we used the C_v expression for such a system. We can use the gas law $PV = nRT$ to translate this expression in one that relates pressure and volume see Eq 19.23

We can mathematically show that the temperature of a gas decreases during an adiabatic expansion. Assuming an ideal gas, the internal energy along an adiabatic path is:

$$\begin{aligned} d\bar{U} &= \delta q + \delta w \\ &= 0 - Pd\bar{V} \\ &= -Pd\bar{V} \end{aligned}$$

The constant volume heat capacity is defined as:

$$\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$$

We can rewrite this for internal energy:

$$d\bar{U} = \bar{C}_V dT$$

Combining these two expressions for internal energy, we obtain:

$$\bar{C}_V dT = -Pd\bar{V}$$

Using the ideal gas law for pressure of an ideal gas:

$$\bar{C}_V dT = -\frac{RT}{\bar{V}} d\bar{V}$$

Separating variables:

$$\frac{\bar{C}_V}{T} dT = -\frac{R}{\bar{V}} d\bar{V}$$

This is an expression for an ideal path along a reversible, adiabatic path that relates temperature to volume. To find our path along a PV surface for an ideal gas, we can start in TV surface and convert to a PV surface. Let's go from (T_1, V_1) to (T_2, V_2).

$$\int_{T1}^{T_2} \frac{\bar{C}_V}{T} dT = -\int_{\bar{V}_1}^{\bar{V}_2} \frac{R}{\bar{V}} d\bar{V}$$

$$\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R\ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) = R\ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{\bar{C}_V}\ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\frac{R}{\bar{C}_V}}$$

We know that:

$$R = \bar{C}_P - \bar{C}_V$$

$$\frac{R}{\bar{C}_V} = \frac{\bar{C}_P - \bar{C}_V}{\bar{C}_V} = \frac{\bar{C}_P}{\bar{C}_V} - 1$$

$$\frac{R}{\bar{C}_V} = \gamma - 1$$

Therefore:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\gamma-1}$$

This expression shows that volume and temperature are inversely related. That is, as the volume increase from V_1 to V_2, the temperature must decrease from T_1 to T_2.

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1.7: Enthalpy and Pressure-Volume Work

Enthalpy

An important point is that pressure-volume work $-PdV$ is only one kind of work. It is the important one for gases but for most other systems we are interested in other kinds of work (e.g. electrical work in a battery).

A good way to measure ΔU's is to make sure there are no work terms at all. If so:

$$\Delta U_{nowork} = q + w = q + 0 = q$$

However, this means that the $-PdV$ volume work term should also be zero and this implies we must keep volumes the same. That can actually be hard. Therefore we define at new state function ENTHALPY

$$H \equiv U + PV$$

(The $\equiv$ symbol is used to show that this equality is actually a definition.)

If we differentiate we get:

$$dH = dU + d(PV) = dU + PdV + VdP$$

We know that under reversible conditions we have

$$dU = \delta w + \delta q = -PdV + \delta q$$

(+ other work terms that we assume zero)

Thus,

$$dH = -PdV + \delta q + PdV + VdP$$

$$dH = \delta q + VdP$$

That means that as long as there is no other work and we keep the pressure constant:

$$\Delta H = q_P$$

instead of

$$\Delta U = q_V$$

Working at constant P is a lot easier to do than at constant V. This means that the enthalpy is a much easier state function to deal with than the energy U.

For example when we melt ice volumes change whether we like or not, but at long as the weather does not change too much pressure is constant. So if we measure how much heat we need to add to melt a mole of ice we get the molar heat of fusion:

Such enthalpies are measured and tabulated.

In this case the volume change is actually quite small, as it usually is for condensed matter. Only if we are dealing with gases is the difference between enthalpy and energy really important

So, U H for condensed matter, but U and H differ for gases.

A good example of this is the difference between the heat capacity at constant V and at constant P. For most materials there is not much of a difference, but for an ideal gas we have

$$C_p = C - V + nR$$

Needless to say that the heat capacity is a path function: it depends on what you keep constant.

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1.8: Heat Capacity is a Path Function

Determining enthalpies from heat capacities.

The functions H and C_p are related by differentiation:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

This means that we can:

1. measure C_p as a function of temperature
2. integrate this function and find $H(T)$

However, there are problems with this approach:

1. Reference point: we have to deal with the lower limit of integration.

   Ideally we start at zero Kelvin (but we cannot get there), but how do we compare one compound to the other?

2. At temperatures where there is a phase transition there is a sudden jump in enthalpy. E.g. when ice melts we have to first add the heat of fusion until all ice is gone before the temperature can go up again (assuming all is done under reversible well-equilibrated conditions).
3. At the jumps in H, the C_p is infinite.

> *It should be stressed that there **are no absolute enthalpies**.*

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1.9: Relative Enthalpies Can Be Determined from Heat Capacity Data and Heats of Transition

It should be stressed that there **are no absolute enthalpies**. All that is properly defined are differences in enthalpy ΔH and these are only defined for ***processes***

When dealing with enthalpies

Define the Process

For example for the process of:

Process 1: ***heating ice from -20°C to -0°C***

We could write $\Delta H_1 = \int C_{P,ice}.\ dT$ from T=253K to T=273K = H(273) -H(253). But before moving beyond the melting point first a different process needs to take place, that of

Process 2: ***melting***

This gives us $\Delta_{fus}H = H_{liquid} - H_{solid}$ (both at 273K!). When we heat the liquid water further to say +20°C we would have to integrate over the heat capacity of the liquid.

Process 3: ***heating water from 0°C to +20°C***

We could write

$$\Delta H_3 = \int C_{P,water} dT$$

from T=273K to T=293K = H(293)-H(273).

The total change in enthalpy between -20 and +20 would be the sum of the three enthalpy changes.

$$\Delta H_{totalprocess} = \Delta H_1 + \Delta_{fus}H + \Delta H_3$$

Of course we could consider doing the same calculation for any temperature between -20 and +20 and summarize all our results in a graph. The three processes can thus schematically be shown in Figure 19.10.1 .

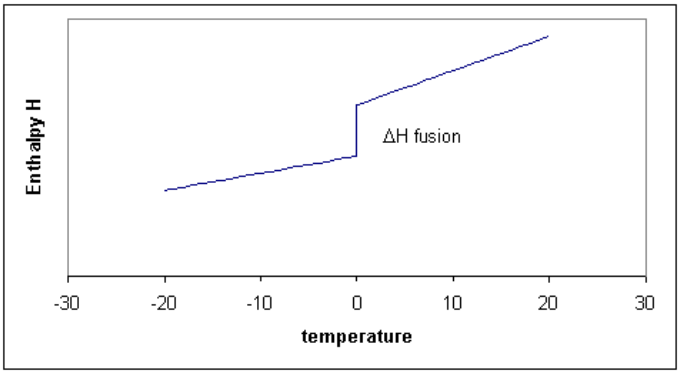


Figure 19.10.1 *: Schematic enthalpy function showing the jump at the melting point*

Notice that the slopes (i.e. the heat capacities!) before and after the melting point differ. The slope for the liquid is a little steeper because the liquid has more degrees of freedom and therefore the heat capacity of the liquid tends to be higher than of the solid. In the figure the enthlapy curves are shown as straight lines. This would be the case if the heat capacities are *constant* over the temperature interval. Although C_p is typically a 'slow' or 'weak' function of temperature it usually does change a bit, which means that the straight lines for H become curves.

> *Although C_p is typically a 'slow' or 'weak' function of temperature and is well approximated as a constant.*

Notice that for process two, the temperature is constant, that means that ΔT or dT is zero, but ΔH is finite, consequently ΔH/ΔT is infinitly large. Taking the limit for ΔT going to zero, we get a derivative:

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

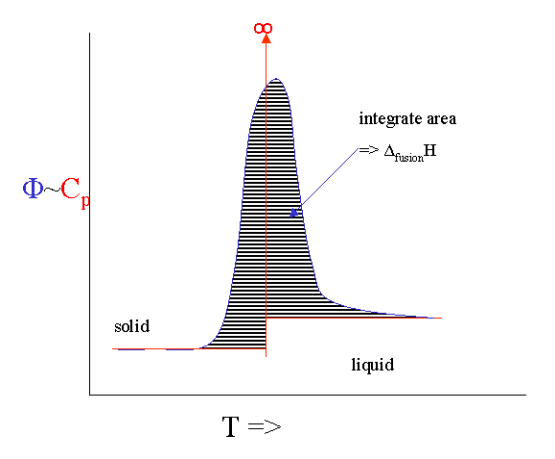
This derivative, the heat capacity must undergo a singularity: the slope is infinitely large (i.e, the H curve goes straight up). When there are more phase transitions, more discontinuities in H and singularities in C_p result (Figure 19.10.1). Note that $H(T) - H(0)$, not $H(T)$ is plotted to avoid the question what the absolute enthalpy is.

Scanningcalorimetry

There is technique that allows us to measure the heat capacity as a function of temperature fairly directly. It is called Differential Scanning Calorimetry (DSC). You put a sample in a little pan and put the pan plus an empty reference pan in the calorimeter. The instrument heats up both pans with a constant heating rate. Both pans get hotter by ***conduction***, but the heat capacity of the filled pan is obviously bigger. This means that the heat flow into the sample pan must be a bit bigger than into the empty one. This differential heat flow induces a tiny temperature difference ΔT between the two pans that can be measured. This temperature difference is proportional to the heat flow difference which is proportional to the heat capacity difference.

$$\Delta T\ \Delta\Phi\ \Delta_{betweenpans} C_p = C_p^{sample}\ (if the pans cancel)$$

However, there are number of serious broadening issues with the technique. If you melt something you will never get to see the infinite singularity of the heat capacity. Instead it broadens out into a peak. If you integrate the peak you get the $\Delta_{fusion}H$ and the onset is calibrated to give you the melting point.



The ideal heat capacity signal and its broadened DSC signal

It is even possible to heat the sample with a rate that fluctuates with a little sine wave. This "Modulated DSC" version can even give you the (small) difference in C_p before and after the melting event.

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1.10: Enthalpy Changes for Chemical Equations are Additive

Hess's law

As enthalpy and energy are state functions we should expect ***additivity*** of U and H when we study chemical reactions. This additivity is expressed in **Hess's Law**. The additivity has important consequences and the law finds wide spread application in the prediction of heats of reaction.

1. The reverse reaction has the negative enthalpy of the forward one.
2. If we can do a reaction in two steps we can calculate the enthalpy of the combined reaction by adding up:

Reaction	Enthalpy
$C_{(s)}$ + ½ $O_{2(g)}$ -> $CO_{(g)}$	$\Delta_r H$ = -110.5 kJ
$CO_{(g)}$ + ½ $O_{2(g)}$ -> $CO_{2(g)}$	$\Delta_r H$ = -283.0 kJ
This means that	----------+
$C_{(s)}$ + O2(g) -> CO2(g)	$\Delta_r H$ = -393.5 kJ

By this mechanism it is often possible to calculate the heat of a reaction even if this reaction is hard to carry out. E.g. we could burn both graphite and diamond and measure the heats of combustion for both. The difference would give us the heat of the transformation reaction from graphite to diamond.

Reaction-as-written convention (caution!)

The enthalpy is for the ***reaction-as-written***. That means that if we write:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

with $\Delta_r H$ = -221 kJ (***not***: -110.5 kJ)

Reverse reactions

Because H is a state function the reverse reaction has the same enthalpy but with opposite sign

$$2CO(g) \rightarrow 2C(s) + O_2(g)$$

with $\Delta_r H$ = +221 kJ

Combining values

It is quite possible that you cannot really do a certain reaction in practice. For many reactions we can arrive at enthalpy values by doing some bookkeeping. For example, we can calculate the enthalpy for the reaction of PCl_3 with chlorine if we know the two reactions that the elements phosphorous and chlorine can undergo.

> *You do have to make sure you balance your equations properly!*

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1.11: Heats of Reactions Can Be Calculated from Tabulated Heats of Formation

Reaction enthalpies are important, but difficult to tabulate. However, because enthalpy is a state function, it is possible to use **Hess' Law** to simplify the tabulation of reaction enthalpies. Hess' Law is based on the addition of reactions. By knowing the reaction enthalpy for constituent reactions, the enthalpy of a reaction that can be expressed as the sum of the constituent reactions can be calculated. The key lies in the canceling of reactants and products that °Ccur in the "data" reactions but not in the "target reaction.

Example 1.11.1:

Find ΔH_{rxn} for the reaction

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Given

$$C(gr) + ½O_2(g) \rightarrow CO(g)$$

with $\Delta H_1 = -110.53\,kJ$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_2 = -393.51\,kJ$

Solution

The target reaction can be generated from the data reactions.

$$2\times\ [CO(g) \rightarrow C(gr) + O_2(g)]$$

plus

$$2\times\ [C(gr) + 2O_2(g) \rightarrow 2CO_2(g)]$$

equals

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

so

$$2\times\Delta H_1 = -787.02\,kJ$$

$$2\times\Delta H_2 = 221.06\,kJ$$

$$2\times\Delta H_1 + 2\times\Delta H_2 = -565.96\,kJ$$

Standard Enthalpy of Formation

One of the difficulties with many thermodynamic state variables (such as enthalpy) is that while it is possible to measure changes, it is impossible to measure an absolute value of the variable itself. In these cases, it is necessary to define a zero to the scale defining the variable. For enthalpy, the definition of a zero is that the standard enthalpy of formation of a pure element in its standard state is zero. All other enthalpy changes are defined relative to this standard. Thus it is essential to very carefully define a standard state.

Definition: the Standard State

The standard state of a substance is the most stable form of that substance at 1 atmosphere pressure and the specified temperature.

Using this definition, a convenient reaction for which enthalpies can be measured and tabulated is the **standard formation reaction**. This is a reaction which forms one mole of the substance of interest in its standard state from elements in their standard states. The enthalpy of a standard formation reaction is the **standard enthalpy of formation** (ΔH_{f°). Some examples are

- $NaCl(s)$:

- $NaCl(s)$:

$$Na(s) + ½Cl_2(g) \rightarrow NaCl(s)$$

with $\Delta H_f^o = -411.2\, kJ/mol$

- $C_3H_8(g)$:

$$3C(gr) + 4H_2(g) \rightarrow C_3H_8(g)$$

with $\Delta H_f^o = -103.8\, kJ/mol$

It is important to note that the standard state of a substance is **temperature dependent**. For example, the standard state of water at -10 °C is solid, whereas the standard state at room temperature is liquid. Once these values are tabulated, calculating reaction enthalpies becomes a snap. Consider the heat combustion (ΔH_c) of methane (at 25 °C) as an example.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The reaction can expressed as a sum of a combination of the following standard formation reactions.

$$C(gr) + 2H_2(g) \rightarrow CH_4(g)$$

with $\Delta H_f^o = -74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

with $\Delta H_f^o = -285.8\, kJ/mol$

The target reaction can be generated from the following combination of reactions

$$-1\times [C(gr) + 2H_2(g) \rightarrow CH_4(g)]$$

$$CH_4(g) \rightarrow C(gr) + 2H_2(g)$$

with $\Delta H_f^o = -1\times [-74.6\, kJ/mol] = 74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$2\times [H_2(g) + ½O_2(g) \rightarrow H_2O(l)]$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

with $\Delta H_f^o = 2\times [-285.8\, kJ/mol] = -571.6\, kJ/mol.$

$$CH_4(g) + 2O_2(g) \rightarrow CO2_(g) + 2H_2O(l)$$

with $\Delta H_c^o = -890.5\, kJ/mol$

Alternately, the reaction enthalpy could be calculated from the following relationship

$$\Delta H_{rxn} = \sum_{products} \nu \cdot \Delta H_f^o - \sum_{reactants} \nu \cdot \Delta H_f^o$$

where ν is the stoichiometric coefficient of a species in the balanced chemical reaction. For the combustion of methane, this calculation is

$$\begin{aligned} \Delta_{rxn} &= (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) && (1.11.1)\\ &= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) && (1.11.2)\\ &\quad - (1\, mol)\,(-74.6\, kJ/mol) \\ &= -890.5\, kJ/mol && (1.11.3) \end{aligned}$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization,

fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

with $\Delta H_{rxn} = -890.5\ kJ$. The correct interpretation is that the reaction of one mole of CH_4(g) with two moles of O_2(g) to form one mole of CO_2(g) and two moles of H_2O(l) releases 890.5 kJ at 25 °C.

Ionization Reactions

Ionized species appear throughout chemistry. The energy changes involved in the formation of ions can be measured and tabulated for several substances. In the case of the formation of positive ions, the enthalpy change to remove a single electron at 0 K is defined as the **ionization potential**.

$$M(g) \rightarrow M^+(g) + e^-$$

with $\Delta H(0K) \equiv 1^{st}\ \text{ionization potential (IP)}$

The removal of subsequent electrons requires energies called the 2nd Ionization potential, 3rd ionization potential, and so on.

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

with $\Delta H(0K) \equiv 2^{nd} IP$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$$

with $\Delta H(0K) \equiv 3^{rd} IP$

An atom can have as many ionization potentials as it has electrons, although since very highly charged ions are rare, only the first few are important for most atoms.

Similarly, the **electron affinity** can be defined for the formation of negative ions. In this case, the first electron affinity is defined by

$$X(g) + e^- \rightarrow X^-(g)$$

with $-\Delta H(0K) \equiv 1^{st}\ \text{electron affinity (EA)}$

The minus sign is included in the definition in order to make electron affinities mostly positive. Some atoms (such as noble gases) will have negative electron affinities since the formation of a negative ion is very unfavorable for these species. Just as in the case of ionization potentials, an atom can have several electron affinities.

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$

with $-\Delta H(0K) \equiv 2^{nd} EA$.

$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

with $-\Delta H(0K) \equiv 3^{rd} EA$.

Average Bond Enthalpies

In the absence of standard formation enthalpies, reaction enthalpies can be estimated using average bond enthalpies. This method is not perfect, but it can be used to get ball-park estimates when more detailed data is not available. A **bond dissociation energy** D is defined by

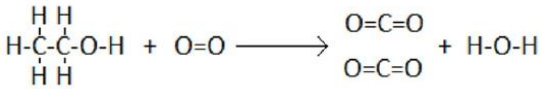
$$XY(g) \rightarrow X(g) + Y(g)$$

with $\Delta H \equiv D(X-Y)$

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H_{rxn} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

As an example, consider the combustion of ethanol:



In this reaction, five C-H bonds, one C-C bond, and one C-O bond, and one O=O bond must be broken. Also, four C=O bonds, and one O-H bond are formed.

Bond	Average Bond Energy (kJ/mol)
C-H	413
C-C	348
C-O	358
O=O	495
C=O	799
O-H	463

The reaction enthalpy is then given by

$$\begin{aligned}\Delta H_c &= 5(413\,kJ/mol) + 1(348\,kJ/mol) + 1(358\,kJ/mol) \\ &\quad + 1(495\,kJ/mol) - 4(799\,kJ/mol) - 2(463\,kJ/mol) \\ &= -856\,kJ/mol\end{aligned} \tag{1.11.4}$$

Because the bond energies are defined for gas-phase reactants and products, this method does not account for the enthalpy change of condensation to form liquids or solids, and so the result may be off systematically due to these differences. Also, since the bond enthalpies are averaged over a large number of molecules containing the particular type of bond, the results may deviate due to the variance in the actual bond enthalpy in the specific molecule under consideration. Typically, reaction enthalpies derived by this method are only reliable to within ± 5-10%.

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- **3.6: Reaction Enthalpies** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

1.12: The Temperature Dependence of ΔH

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$$dH = C_p\,dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_2}^{T_2} C_p\,dT \tag{1.12.1}$$

Equation 1.12.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p\,\Delta T \tag{1.12.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 1.12.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{1.12.3}$$

After combining Equations 1.12.3 and 1.12.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \tag{1.12.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T}\right]_{T_1}^{T_2} \tag{1.12.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1.12.6}$$

This expression can then be used with experimentally determined values of a, b, and c, some of which are shown in the following table.

Table **1.12.1:** *Empirical Parameters for the temperature dependence of* C_p

Substance	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c (J mol^{-1} K)
C(gr)	16.86	4.77 x 10^{-3}	-8.54 x 10^{5}
CO_2(g)	44.22	8.79 x 10^{-3}	-8.62 x 10^{5}
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77 x 10^{-3}	-5.0 x 10^{4}
Pb(s)	22.13	1.172 x 10^{-2}	9.6 x 10^{4}

Example 1.12.1: Heating Lead

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution

The enthalpy change is given by Equation 1.12.1 with a temperature dependence C_p given by Equation 1.12.1 using the parameters in Table **1.12.1**. This results in the integral form (Equation 1.12.6):

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

when substituted with the relevant parameters of Pb(s) from Table **1.12.1**.

$$\begin{aligned}\Delta H =& (22.14\,\frac{J}{mol\,K}(353\,K - 273\,K) \\ &+ \frac{1.172 \times 10^{-2}\frac{J}{mol\,K^2}}{2}\left((353\,K)^2 - (273\,K)^2\right) \\ &- 9.6 \times 10^4 \frac{J\,K}{mol}\left(\frac{1}{(353\,K)} - \frac{1}{(273\,K)}\right) \\ \Delta H =& 1770.4\,\frac{J}{mol} + 295.5\,\frac{J}{mol} + 470.5\,\frac{J}{mol} \\ =& 2534.4\,\frac{J}{mol}\end{aligned}$$

For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

$$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta C_p \Delta T$$

Example 1.12.2: Enthalpy of Formation

The enthalpy of formation of NH_3(g) is -46.11 kJ/mol at 25 ^oC. Calculate the enthalpy of formation at 100 ^oC.

Solution

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

with $\Delta H\,(298\,K) = -46.11\,kJ/mol$

Compound	Cp (J mol^{-1} K^{-1})
N_2(g)	29.12
H_2(g)	28.82
NH_3(g)	35.06

$$\begin{aligned}\Delta H(373\,K) &= \Delta H(298\,K) + \Delta C_p \Delta T \\ &= -46110 + \frac{J}{mol} \\ &\quad \left[2\left(35.06\frac{J}{mol\,K}\right) - \left(29.12\,\frac{J}{mol\,K}\right) - 3\left(28.82\,\frac{J}{mol\,K}\right)\right](373\,K - 298\,K) \\ &= -49.5\,\frac{kJ}{mol}\end{aligned}$$

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1.13: Enthalpy is a State Function

Our expression for internal energy at constant pressure:

$$\Delta U = q_P + w = q_P - P\Delta V$$

Rearrange:

$$q_P = \Delta U + P\Delta V = U_2 - U_1 + P(V_2 - V_1)$$

$$q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

We can define this term as enthalpy:

$$H \equiv U + PV$$

This is a new state function.

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CHAPTER OVERVIEW

2: Entropy, Second and Third Laws

2.1: Energy Does not Determine Spontaneity
2.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal
2.3: Unlike heat, Entropy is a State Function
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2.9: Entropy Increases with Increasing Temperature

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2.1: Energy Does not Determine Spontaneity

There are many spontaneous events in nature. If you open the valve in both cases a spontaneous event occurs. In the first case the gas fills the evacuated chamber, in the second the gases will mix. The state functions U and H do not give us a clue what will happen. You might think that only those events are spontaneous that produce heat.

Not so:

- If you dissolve KNO_3 in water, it does so spontaneously, but the solution gets ***cold***.
- If you dissolve KOH in water, it does so spontaneously, but the solution gets ***hot***.

Clearly the first law is not enough to describe nature.

Two items left on our wish list

Enthalpy alone is not enough to give us a complete understanding of how heat and work are related. Two concerns remain:

1. the spontaneity problem

   we now have a criterion for spontaneity for isolated systems

2. the asymmetry between work->heat (dissipation) and heat->work (power generation)

   at least we can use the new state law to predict the limitations on the latter.

Therefore, we suspect that there is a new state function that can serve as a spontaneity criterion *for all systems* (not just isolated ones). We will find such a state function and call it entropy, or *S*.

Entropy on a microscopic scale

Let us start with the latter. Yes we can use S to explain the odd paradox between w and q both being forms energy on the one hand, but the conversion being easier in one direction than the other, but we have introduced the concept *entropy* purely as a phenomenon on iis own. Scientifically there is nothing wrong with such a phenomenological theory except that experience tells us that if you can understand the phenomenon itself better your theory becomes more powerful.

To understand entropy better we need to leave the macroscopic world and look at what happens on a molecular level and do statistics over many molecules. First, let us do a bit more statistics of the kind we will need.

Permutations

If we have n distinguishable objects, say playing cards we can arrange them in a large number of ways. For the first object in our series we have n choices, for number two we have $n-1$ choices (the first one being spoken for) etc. This means that in total we have

$$W = n(n-1)(n-2)\ldots.4.3.2.1 = n! \text{ choices.}$$

The quantity W is usually called the number of realizations in thermodynamics.

The above is true if the objects are all distinguishable. If they fall in groups within which they are not distinguishable we have to correct for all the swaps within these groups that do not produce a distinguishably new arrangement. This means that W becomes $\frac{n!}{a!b!c!\ldots z!}$ where a,b, c to z stands for the size of the groups. (Obviously $a+b+c+..+z=n$)

In thermodynamincs our 'group of objects' is typically an ensemble of systems, think of size N_{av} and so the factorial become horribly large. This makes it necessary to work with logarithms. Fortunately there is a good approximation (by Stirling) for a logarithmic factorial:

$$\ln N! \approx N \ln N - N$$

Causality vs. Correlation

In Europe nosey little children who are curious to find out where their newborn little brother or sister came from, often get told that the stork brought it during the night. When you look at the number of breeding pairs of this beautiful bird in e.g. Germany since 1960 you see a long decline to about 1980 when the bird almost got extinct. After that the numbers go up again due to breeding programs mostly. The human birth rate in the country follows a pretty much identical curve and the correlation between the two is very high (>0.98 or so). (Dr H. Sies in Nature (volume 332 page 495; 1988). Does this prove that storks indeed bring babies?



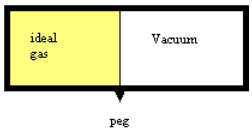
An adult White Stork. from Wikipedia (credit: Frank Vassen).

Answer:

No, it does ***not*** show causality, just a correlation due a common underlying factor. In this case that is the choices made by the German people. First they concentrated on working real hard and having few children to get themselves out of the poverty WWII had left behind and neglected the environment, then they turned to protect the environment and opened the doors to immigration of people, mostly from Muslim countries like Turkey or Morocco, that usually have larger families. The lesson from this is that you can only conclude causality ***if*** you are sure that there are no other intervening factors.

Changing the size of the box with the particles in it

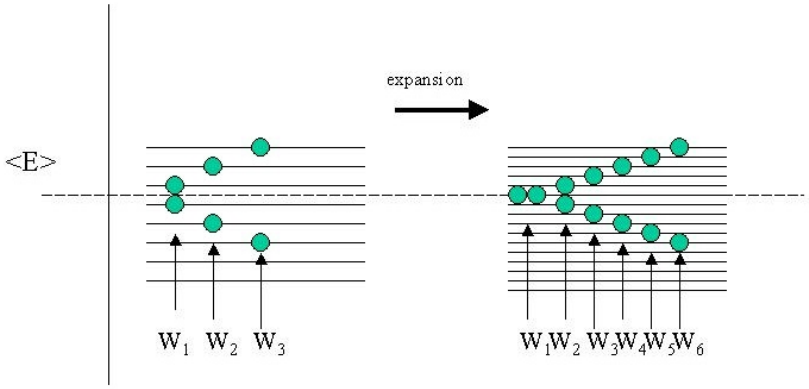
The expansion of an ideal gas against vacuum is really a wonderful *model experiment*, because *nothing else happens* but a spontaneous expansion and a change in entropy. No energy change, no heat, no work, no change in mass, no interactions, nothing. In fact, it does not even matter whether we consider it an isolated process or not. We might as well do so.



Physicists and Physical Chemists love to find such experiments that allows them to retrace *causality*. All this means that if we look at what happens at the atomic level, we should be able to retrace the ***cause*** of the entropy change. As we have seen before, the available energy states of particles in a box depend on the size of the box.

$$E_{kin} = \frac{h^2}{8ma^2}\left[n_1^2 + n_2^2 + n_2^2\right]$$

Clearly if the side (a and therefore the volume of the box changes, the energy spacing between the states will become smaller. Therefore during our expansion against vacuum, the energy states inside the box are changing. Because U does not change the *average* energy $\langle E \rangle$ is constant. Of course this average is taken over a great number of molecules (*systems*) in the gas (the *ensemble*), but let's look at just two of them and for simplicity let us assume that the energy of the states are equidistant (rather than quadratic in the quantum numbers n).



As you can see there is more than one way to skin a cat, or in this case to *realize* the same average $\langle E \rangle$ of the complete ensemble (of only two particles admittedly). Before expansion I have shown three realizations W_1, W_2, W_3 that add up to the same $\langle E \rangle$. After expansion however, there are more energy states available and the schematic figure shows twice as many realizations W in the same energy interval.

Boltzmann was the first to postulate that this is what is at the root of the entropy function, not so much the (total) energy itself (that stays the same!), but the number of ways the energy can be distributed in the ensemble. Note that because the ensemble average (or total) energy is identical, we could also say that the various realizations W represent the degree of *degeneracy* Ω of the ensemble.

Boltzmann considered a much larger (*canonical*) ensemble consisting of a great number of identical *systems* (e.g. molecules, but it could also be planets or so). If each of our systems already has a large number of energy states the systems can all have the same (total) energy but distributed in rather different ways. This means that two systems within the ensemble can either have the same distribution or a different one. Thus we can divide the ensemble A in subgroups a_j having the same energy distribution and calculate the number of ways to distribute energy in the ensemble A as

$$W = \frac{A!}{a1!a2!\ldots}.$$

Boltzmann postulated that entropy was directly related to the number of realizations W, that is the number of ways the same energy can be distributed in the ensemble. This leads immediately to the concept of order versus disorder, e.g, if the number of realizations is $W = 1$, all systems must be in the same state (W=A! / A!0!0!0!…) which is a very orderly arrangement of energies.

If we were to add two ensembles to each other the total number of possible arrangements W_{tot} becomes the product W_1W_2 but the entropies should be additive. As logarithms transform products into additions Boltzmann assumed that the relation between W and S should be logarithmic and wrote:

$$S = k \ln W$$

Again, if we consider a very ordered state, e.g. where all systems are in the ground state the number of realizations A!/A!= 1 so that the entropy is zero. If we have a very messy system where the number of ways to distribute energy over the many many different states is very large S becomes very large. Thus entropy is very large.

This immediately gives us the driving force for the expansion of a gas into vacuum or the mixing of two gases. We simply get more energy states to play with, this increases W. This means an increase in S. This leads to a spontaneous process.

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2.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal

In spontaneous processes for an isolated system, there is a competition between minimizing the energy of the system and increasing the dispersal of energy within the system. If energy is constant, then the system will evolve to maximize energy dispersal. If energy dispersal is not a factor, the system will evolve to minimize its energy. We already have a quantitative basis for the energy of a system and we need to do the same for energy dispersal. Suppose we have a small reversible change dU in the energy of an ideal gas. We know that U only depends on temperature:

$$dU = C_v dT$$

We also know that any reversible work would be volume work.

$$\delta w_{rev} = -PdV$$

This means that we can write:

$$\begin{aligned} \delta q_{rev} &= dU - \delta w_{rev} \\ &= C_v dT + PdV \end{aligned}$$

Let us examine if this represents an **exact differential**. If δq were an exact differential, we could write the total differential:

$$\delta q_{rev} = \left(\frac{\partial q}{dT}\right)_V dT + \left(\frac{\partial q}{dV}\right)_T dV$$

And the following would be true:

$$\frac{\partial^2 q_{rev}}{\partial T \partial V} = \frac{\partial^2 q_{rev}}{\partial V \partial T}$$

From our equation above, we know that:

$$\frac{\partial q_{rev}}{\partial T} = C_V$$

$$\frac{\partial q_{rev}}{\partial V} = P$$

Therefore, the following should be true:

$$\frac{\partial C_V}{\partial V} = \frac{\partial P}{\partial T}$$

However,

$$\frac{\partial C_v}{\partial V} = 0$$

Because C_v does not depend on volume (only T, just like U: it is its derivative). And:

$$\frac{\partial P}{\partial T} = \frac{\partial nRT}{\partial T} = \frac{nR}{V}$$

Which is not zero!! Clearly, δq_{rev} is **not a state function**, but look what happens if we multiply everything with an 'integration factor' $1/T$:

$$\frac{\delta q_{rev}}{T} = \frac{C_v}{T} dT + \frac{P}{T} dV$$

$$\frac{\partial C_v/T}{\partial V} = 0$$

Because $\frac{C_v}{T}$ does not depend on volume. However,

$$\frac{\partial(P/T)}{\partial T} = \frac{\partial(nR/V)}{\partial T} = 0$$

Thus, the quantity $dS = \frac{\delta q_{rev}}{T}$ is an exact differential, so S is a state function and it is called **entropy**. Entropy is the dispersal of energy, or equivalently, the measure of the number of possible microstates of a system.

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2.3: Unlike heat, Entropy is a State Function

Circular integrals

Because entropy is a state function, it integrates to zero over any circular path going back to initial conditions, just like U and H:

$$\oint dS = 0$$

$$\oint dH = 0$$

$$\oint dU = 0$$

As discussed previously, we can use this fact to revisit the isotherm + isochore + adiabat circular path (Figure 20.3.1).

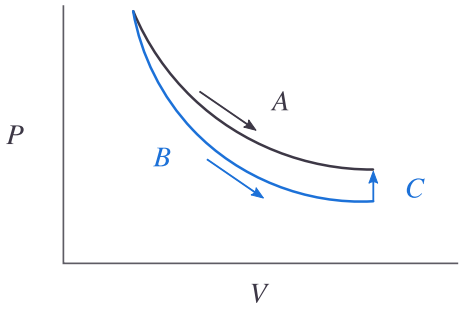


Figure 20.3.1 : A: isothermal expansion, B:adiabat, C:isochore (CC BY-NC; Ümit Kaya via LibreTexts)

Along adiabat B and isochore C:

- There is no heat transfer along adiabat B:

$$q_{rev,B} = 0$$

- There is no work along isochore C:

$$\delta w = 0$$

- But the temperature changes from T_2 back to T_1. This requires heat:

$$q_{rev,C} = C_V \Delta T$$

Along the isotherm A:

- We have seen that

$$q_{rev,A} = nRT \ln \frac{V_2}{V_1}$$

The quantities $q_{rev,A}$, $q_{rev,B}$, and $q_{rev,C}$ are ***not*** the same, which once again underlines that heat is a path function. How about entropy?

First, consider the combined paths of B and C:

$$q_{rev,B+C} = \int_{T_2}^{T_1} C_v dT$$

$$\int dS_{B+C} = \int \frac{dq_{rev,B+C}}{T} = \int_{T_2}^{T_1} \frac{C_v}{T} dT$$

We had seen this integral before from Section 19-6, albeit from T_1 to T_2:

$$\Delta S_{B+C} = nR \ln \frac{V_2}{V_1} \tag{2.3.1}$$

(Notice sign in Equation 2.3.1 is positive)

Along the isotherm A:

$$q_{rev,A} = nRT \ln \frac{V_2}{V_1}$$

T is a constant so we can just divide $q_{rec,A}$ by T to get ΔS_A:

$$\Delta S_A = nR \ln \frac{V_2}{V_1}$$

We took two different paths to get start and end at the same points. Both paths had the same change in entropy. Clearly entropy is a *state function* while q_{rev} is not.

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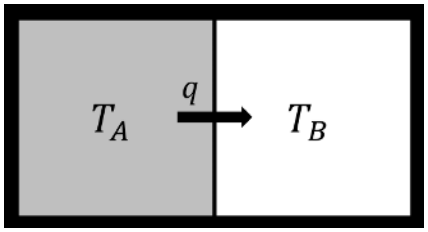
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2.4: The Second Law of Thermodynamics

Spontaneity of an isolated system

> An **isolated system** is a little more than just adiabatic. In the latter heat cannot get in or out. In an isolated system *nothing* gets in or out, neither heat nor mass nor even any radiation, such as light. The isolated system is like a little universe all to itself.

Let us consider a zero law process. We have two identical blocks of metal, say aluminum. They are each at thermal equilibrium, but at different temperatures. They are brought into contact with each other but isolated from the rest of the universe.



- ***Zeroth law***: *Heat will flow from hot to cold*
- ***First law***: *There is no change in total energy*

so:

$$dU_A = -dU_B$$

There is also no work so:

$$dU_A = \delta q_A + 0$$

Because U is a state function this makes q a state function as well, otherwise this equality does not hold. As there is only one term on the right there is only one path (along q). So we could write:

$$dU_A = dq_A$$

This implies that we do not need to worry about reversible and irreversible paths as there is only one path. Since:

$$dS = \frac{\delta q_{rev}}{T}$$

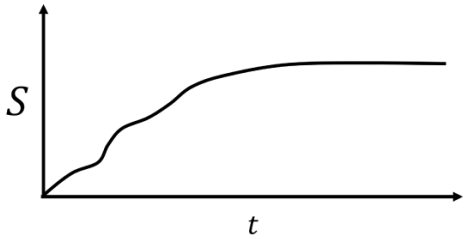
In this particular case:

$$TdS = \delta q_{rev} = dU$$

Thus we get:

$$dS = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} = \frac{dU_A}{T_A} - \frac{dU_A}{T_B} = dU_A\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$$

Clearly as long as the two temperatures are not the same dS is not zero and entropy is not conserved. Instead it is **increasing**. Over time, the temperatures will become the same (if the blocks are identical, the final temperature is the average of T_A and T_B) and the entropy will reach a maximum.



For our two identical blocks of metal (with same heat capacity, C_V), we can, in fact, derive that the entropy change:

$$\Delta S = C_V \ln \left[\frac{T_A^2 + T_B^2}{4 T_A T_B} \right].$$

This is indeed a positive quantity. In general, we can say for an isolated system:

$$dS \geq 0$$

Thus if we are dealing with a spontaneous (and isolated) process $dS > 0$ and ***entropy is being produced***. This gives us a ***criterion for spontaneity***.

Entropy exchange of an open system

In an isolated system dS represents the produced entropy dS_{prod} and this is a good criterion for spontaneity. Of course the requirement that the system is isolated is very restrictive and makes the criterion as good as useless... What happens in a system that can exchange heat with the rest of the universe? We do have entropy changes in that case, but part of them may have nothing to do with production, because we also have to consider the heat that is exchanged.

$$dS = dS_{prod} + dS_{exchange}$$

If the process is reversible (that is completely non-spontaneous) we are dealing with δq_{rev} so that $dS_{exchange} = \delta q_{rev}/T$, but that is also what dS_{tot} is equal to (by definition). This leaves no room for entropy production.

So we have:

Isolated: $dS = dS_{prod} + 0$

Reversible $dS = 0 + \delta q_{rev}/T$

Notice that this demonstrates that for non-isolated systems entropy change is *not* a good criterion for spontaneity at all... In the case the heat exchange is ***irreversible*** *part* of the entropy is entropy production by the system:

Irreversible: $dS = dS_{prod} + \delta q_{irrev}/T$

$dS > \delta q_{irrev}/T$ in this case.

Generalizing the isolated, irreversible and reversible cases we may say:

$$dS \geq \frac{\delta q}{T}$$

This is the ***Clausius inequality***.

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2.5: The Famous Equation of Statistical Thermodynamics is S=k ln W

A common interpretation of entropy is that it is somehow a measure of chaos or randomness. There is some utility in that concept. Given that entropy is a measure of the dispersal of energy in a system, the more chaotic a system is, the greater the dispersal of energy will be, and thus the greater the entropy will be. Ludwig Boltzmann (1844 – 1906) (O'Connor & Robertson, 1998) understood this concept well, and used it to derive a statistical approach to calculating entropy. Boltzmann proposed a method for calculating the entropy of a system based on the number of energetically equivalent ways a system can be constructed.

Boltzmann proposed an expression, which in its modern form is:

$$S = k_b \ln(W) \tag{2.5.1}$$

W is the number of available microstates in a macrostate (ensemble of systems) and can be taken as the quantitative measure of energy dispersal in a macrostate:

$$W = \frac{A!}{\prod_j a_j!}$$

Where a_j is the number of systems in the ensemble that are in state j and A represents the total number of systems in the ensemble:

$$A = \sum_j a_j$$

Equation 20.5.1 is a rather famous equation etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure 2.5.1).



Figure 2.5.1: Ludwig Boltzmann (1844 - 1906)

Example 2.5.1:

Calculate the entropy of a carbon monoxide crystal, containing 1.00 mol of CO, and assuming that the molecules are randomly oriented in one of two equivalent orientations.

Solution:

Using the Boltzmann formula (Equation 2.5.1):

$$S = nK \ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$S = \left(1.00\,mol \cot \frac{6.022 \times 10^{23}}{1\,mol}\right)(1.38 \times 10^{-23} J/K) \ln 2$$
$$= 5.76\,J/K$$

Contributors and Attributions

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)
- Jerry LaRue (Department of Chemistry and Biochemistry, Chapman University)

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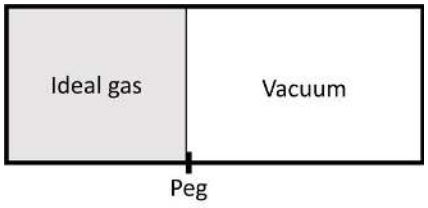
2.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes

The second law of thermodynamics can be formulated in many ways, but in one way or another they are all related to the fact that the state function entropy, S, tends to increase over time in isolated systems. For a long time, people have looked at the entire universe as an example of an isolated system and concluded that its entropy must be steadily increasing until $\delta S_{universe}$ becomes zero. As we will see below, the second law has important consequences for the question of how we can use heat to do useful work.

> Of late, cosmologists like the late Richard Hawkins have begun to question the assumption that the entropy of the universe is steadily increasing. The key problem is the role that gravity and relativity play in creating black holes.

Vacuum Expansion

Let's compare two expansions from V_1 to V_2 for an ideal gas, both are isothermal. The first is an irreversible one, where we pull a peg an let the piston move against vacuum:



The second one is a reversible isothermal expansion from V_1 to V_2 (and P_1 to P_2) that we have examined before. In both cases, the is no change in internal energy since T does not change. During the irreversible expansion, however, there is also no volume work because the piston is expanding against a vacuum and the following integral:

$$\int -P_{ext} dV = 0$$

integrates to zero. The piston has nothing to perform work against until it slams into the right hand wall. At this point $V = V_2$ and then dV becomes zero. This is not true for the reversible isothermal expansion as the external pressure must always equal the internal pressure.

> *No energy and no work means no heat!*

Clearly the zero heat is irreversible heat ($q_{irr} = 0$) and this makes it hard to calculate the entropy of this spontaneous process. But then this process ends in the same final state as the reversible expansion from V_1 to V_2. We know that dU is still zero, but now $\delta w_{rev} = -\delta q_{rev}$ is nonzero. We calculated its value before:

$$q_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right) \tag{2.6.1}$$

The Claussius definition of entropy change can be used to find ΔS (under constant temperature).

$$\Delta S = \frac{q_{rev}}{T} \tag{2.6.2}$$

Substituting Equation 2.6.1 into Equation 2.6.2 results in

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

As S is a state function this equation also holds for the irreversible expansion against vacuum.

> Always calculate the entropy difference between two points along a **reversible** path.

For the irreversible expansion into vacuum we see that

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) + 0 \\ &= nR\ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

For the reversible expansion, heat is transferred to the system while the system does work on the surroundings in order to keep the process isothermal:

$$\Delta S_{\text{sys}} = nR\ln\left(\frac{V_2}{V_1}\right)$$

The entropy change for the surrounding is the opposite of the system:

$$\Delta S_{\text{surr}} = -nR\ln\left(\frac{V_2}{V_1}\right)$$

This is because the amount of heat transferred to the system is the same as the heat transferred from the surroundings and this process is reversible so the system and surroundings are at the same temperature (equilibrium). Heat is related to entropy by the following equation:

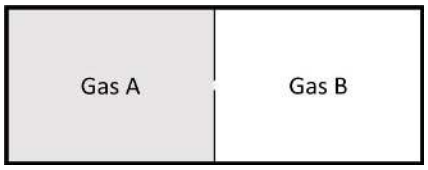
$$dS = \frac{\delta q}{T}$$

Therefore, the total entropy change for the reversible process is zero:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_2}{V_1}\right) \\ &= 0\end{aligned}$$

The Mixing of Two Gases

Consider two ideal gases at same pressure separated by a thin wall that is punctured. Both gases behave as if the other one is not there and again we get a spontaneous process, mixing in this case.



If the pressure is the same the number of moles of each gas should be proportional to the original volumes, V_A and V_B, and the total number of moles to the total volume V_{tot}.

For gas A we can write:

$$\Delta S_A = n_A R\ln\frac{V_{tot}}{V_A} = n_A R\ln\frac{n_{tot}}{n_A}$$

and similarly for gas B we can write:

$$\Delta S_B = n_B R\ln\frac{V_{tot}}{V_B} = n_B R\ln\frac{n_{tot}}{n_B}$$

The total entropy change is therefore the sum of constituent entropy changes:

$$\Delta S = \Delta S_A + \Delta S_B$$

and the entropy change total per mole of gas is:

$$\frac{\Delta S}{n_{tot}} = R\frac{\left[n_B\ln\frac{n_{tot}}{n_B} + n_A\ln\frac{n_{tot}}{n_A}\right]}{n_{tot}} \tag{2.6.3}$$

Equation 2.6.3 can be simplified using mole fractions:

$$\chi_A = \frac{n_A}{n_{tot}}$$

and the mathematical relationship of logarithms that:

$$\ln\left(\frac{x}{y}\right) = -\ln\left(\frac{y}{x}\right)$$

to:

$$\Delta\bar{S} = -R\left[\chi_A \ln \chi_A + \chi_B \ln \chi_B\right] \tag{2.6.4}$$

In the case of mixing of more than two gases, Equation 2.6.4 can be expressed as:

$$\Delta\bar{S} = -R\sum \chi_i \ln \chi_i \tag{2.6.5}$$

This entropy expressed in Equations 2.6.4 and 2.6.5 is known as the **entropy of mixing**; its existence is the major reason why there is such a thing as diffusion and mixing when gases, and also solutions (even solid ones), are brought into contact with each other.

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2.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

Heat and work are both forms of transferring energy, and under the right circumstance, one form may be transformed into the other. However, the second law of thermodynamics puts a limitation on this. To go from work to heat is called dissipation and there is no limitation on this at all. In fact it was through dissipation (by friction) that we discovered that heat and work were both forms of energy. There is, however, a limitation on converting heat to work.

The Carnot Cycle

Let's consider a circular, reversible path of an ideal gas on a PV diagram in Figure **2.7.1**:

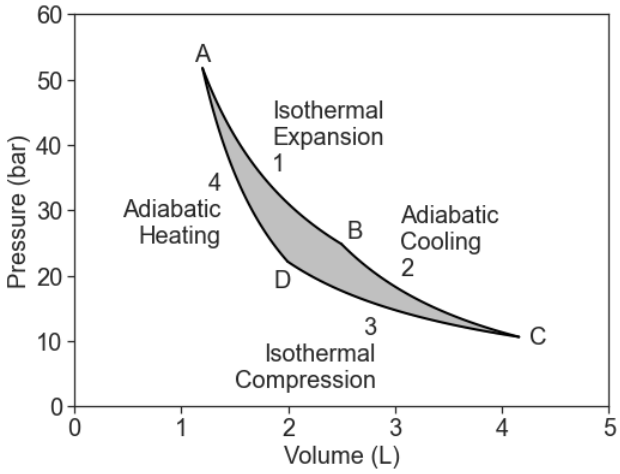


Figure **2.7.1**: A circular, reversible path of a Carnot cycle as an ideal gas on a PV diagram. (CC BY 4.0; Jerry LaRue via LibreTexts)

This cycle forms the 4-stage Carnot cycle heat engine. A heat engine converts heat energy into work. The cycle consists of:

1. Isothermal expansion at the hot temperature, T_h:

$$\Delta U_1 = w_1 + q_h = 0$$

2. Adiabatic cooling from T_h to T_c:

$$\Delta U_2 = w_2$$

3. Isothermal compression at the cold temperature, T_c:

$$\Delta U_3 = w_3 + q_c = 0$$

4. Adiabatic heating from T_c to T_h:

$$\Delta U_4 = w_4$$

The total four-step process produces work because $w_{hot} > w_{cold}$. The work is the integral under the upper isotherm minus the one under the lower curve, i.e. the surface *area in between*.

Sadi Carnot

Sadi Carnot was a French engineer at the beginning of the 19th century. He considered a cyclic process involving a cylinder filled with gas. This cycle the Carnot cycle contributed greatly to the development of thermodynamics and the improvement of the steam engine. Carnot demonstrated that the cold temperature on the right is as important as the heat source on the left in defining the possible efficiency of a heat engine

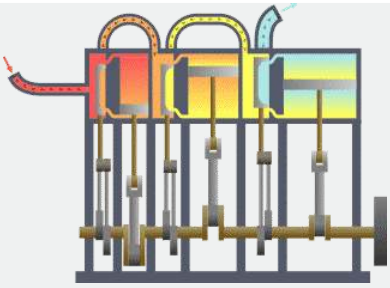


Figure **2.7.2**: Animation of a typical vertical triple-expansion engine. (CC SA-BY 2.5; Emoscopes)

Efficiency

Of course we spend good money on the fuel to start the cycle by heating things up. So how much work do we get for the heat we put in? In other words, we want to know how efficient our heat engine is. The efficiency, η of a heat engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

To get the work of the cycle, we can make use of internal energy as a state function. As the path is circular the circular integrals for U is zero:

$$\begin{aligned} \oint dU &= \Delta U_{\text{cycle}} \\ &= \sum \Delta U_i \\ &= w_1 + q_h + w_2 + w_3 + q_c + w_4 \\ &= 0 \end{aligned}$$

Rearranging:

$$\begin{aligned} q_h + q_c &= -w_1 - w_2 - w_3 - w_4 \\ &= -w_{\text{cycle}} \end{aligned}$$

An ideal engine would take $q_h \to q_c$ with 100% efficiency. The work of the cycle will be equivalent to the heat transfer. For ideal gases:

1. $w_1 = -RT_h \ln\left(\frac{V_B}{V_A}\right) = -q_h$
2. $dU = \delta w = \bar{C}_V dT \to w_2 = \bar{C}_V (T_c - T_h)$
3. $w_3 = -RT_c \ln\left(\frac{V_D}{V_C}\right) = -q_c$
4. $w_4 = \bar{C}_V (T_h - T_c)$

Finding an expression for w_{cycle}:

$$\begin{aligned} w_{\text{cycle}} &= -RT_h \ln\left(\frac{V_B}{V_A}\right) + \bar{C}_V (T_c - T_h) - RT_c \ln\left(\frac{V_D}{V_C}\right) + \bar{C}_V (T_h - T_c) \\ &= -RT_h \ln\left(\frac{V_B}{V_A}\right) - RT_c \ln\left(\frac{V_D}{V_C}\right) = -R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right) \end{aligned}$$

We have an expression for work, so we can evaluate the efficiency, η. The efficiency of the Carnot engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)}{RT_h \ln\left(\frac{V_B}{V_A}\right)} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

Paths (2) and (4) are adiabats, so we can also use entropy, S, to get the same solution:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

Therefore:

$$\frac{q_c}{q_h} = -\frac{T_c}{T_h}$$

And we get that:

$$\eta = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \tag{2.7.1}$$

As you see we can only get full efficiency if T_{cold} is 0 K, which is never (i.e., we always waste energy). Another implication is that if $T_c = T_h$ then **no work** can be obtained, no matter how much energy is available in the from of heat. Or in other words, if one dissipates work into heat isothermally, *none* of it can be retrieved. Equation 2.7.1 is not very forgiving at all. Just imaging that you have a heat source of say 400 K (a superheated pool of water, e.g. a geyser) and you are dumping in the river at room temperature 300 K. The best efficiency you'll ever get is:

$$\eta = 1 - \frac{300}{400} = 24\%$$

Sadly, you'd be dumping three quarters of your energy as heat in the river (and that is best case scenario as there are always more losses, e.g. due to friction). The arrow saying Q_C in Figure 2.7.3 should then be three times as fat as the one that says w.

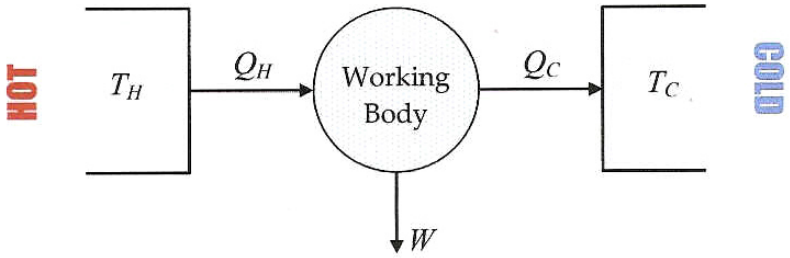


Figure 2.7.3: Carnot engine diagram (modern) - where an amount of heat Q_H flows from a high temperature $T_H$furnace through the fluid of the "working body" (working substance) and the remaining heat Q_C flows into the cold sink T_C, thus forcing the working substance to do mechanical work W on the surroundings, via cycles of contractions and expansions. (Public Domain; Eric Gaba)

Heat pumps

So getting our work from heat is hard and always less than 100% successful. The other way around should be easy. After all, we can dissipate work into heat freely even under isothermal conditions!

What happens if we let the heat engine run backwards? Consider reversing all the flows in the above diagram. Obviously we must *put in work* to make the cycle run in reverse. The heat will now flow from cold to hot, say from your cold garden into your nice and warm apartment. The amount of heat you get in your humble abode will be the sum of all the work (say 100 Joules) you dissipate *plus* the heat you pumped out of the garden (say 300 Joules). Thus if you are willing to pay for the energy you dissipate (100 Joules), you may well end up with a total of 400 Joules of heat in your apartment! Obviously if it is heat you after this is a better deal than just dissipating the work in your apartment (by burning some oil). Then you'd only get 100 J for your precious buck.

Dissipating it as electrical heating is even worse because you would

1. first burn (a lot more!) oil to generate heat
2. use this heat to produce electrical work at great expense because a lot of the heats gets dumped at the low temperature side (the river or so)
3. dissipate the work again in your apartment (without using it to pump any heat out of the garden)

Refrigerators are also heat pumps. They heat the kitchen by pumping heat from its innards to the kitchen. If I keep the door open, however, all it does is dissipate precious electrical work, because the pumped heat will flow back into its innards and spoil the milk.

Stirling Engine

Let's consider another type of heat engine, the Stirling engine. The Stirling engine uses a circular reversible path in an ideal PV diagram in Figure 2.7.4:

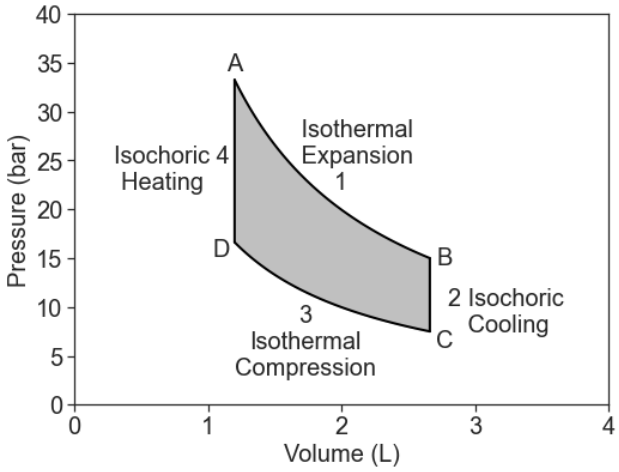


Figure **2.7.4**: an ideal PV diagram of the Stirling engine. (CC BY 4.0; Jerry LaRue via LibreTexts)

The path consists of four steps:

1. *Isothermal* expansion at the hot temperature T_h:

   $$q_1 = q_h = -w$$

   and we get work **out** (i.e., negative work):

   $$w_h = -RT_h \ln\left(\frac{V_B}{V_A}\right)$$

2. *Isochoric* heating from T_c to T_h (with constant C_V):

   $$q_2 = \frac{C_V}{\Delta T} \tag{2.7.2}$$

3. *Isothermal* compression at the cold temperature T_c:

   $$q_3 = q_c = -w$$

   and we must put work **in** (i.e., positive work):

   $$w_c = -RT_c \ln\left(\frac{V_D}{V_C}\right) = RT_c \ln\left(\frac{V_B}{V_A}\right)$$

4. *Isochoric* cooling from T_h to T_c (with constant C_V):

   $$q_4 = -\frac{C_V}{\Delta T} \tag{2.7.3}$$

Notice that this gray area *vanishes* if $T_h = T_c$. Obviously how cold the cold side is of great importance! The amount of work is also equal to the difference in the heat picked up at high temperature q_h and dumped at low temperature q_c. The isochoric heats cancel. The problem is that q_c is only zero if the cold temperature is 0 K. That means that we can never get all the heat we pick up at high temperatures to come out as work.

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2.8: The 3rd Law of Thermodynamics Puts Entropy on an Absolute Scale

Learning Objectives

- Recall the third law of thermodynamics.

In the unlikely case that we have C_p data all the way from 0 K we could write:

$$S(T) = S(0) + \int_0^T C_p(T)\, dT$$

It is tempting to set the $S(0)$ to zero and make the entropy thus an absolute quantity. As we have seen with enthalpy, it was not really possible set $H(0)$ to zero. All we did was define ΔH for a particular process, although if C_p data are available we could construct an enthalpy function (albeit with a floating zero point) by integration of C_P (instead of C_p/T!). The situation is different for entropy S than for H. Here we can actually put things on an ***absolute*** scale. Both Nernst and Planck have proposed to do so. Nernst postulated that for a pure and perfect crystal S should indeed to go to zero as T goes to zero (Figure 2.8.1).

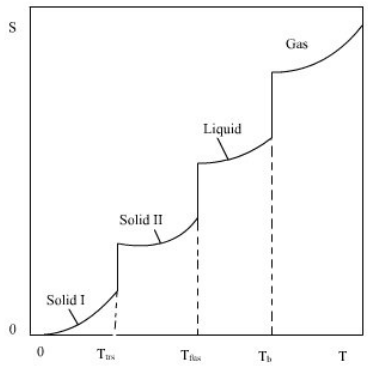


Figure 2.8.1: Entropy as a Function of Temperature. The entropy (S) of a substance (compound or element) as a function of temperature (T). Note that there are three phase transitions in this system with evolution through two solid phases. These result in positive jumps in the entropy.

Example 2.8.1: Sulfur

Sulfur has two solid crystal structure, rhombic and monoclinic. At 368.5 K, the entropy of the phase transition from rhombic to monoclinic, $S_{(rh)} \rightarrow S_{(mono)}$, is:

$$\Delta_{trs} S(368.5\ \text{K}) = 1.09\ \frac{\text{J} \cdot \text{mol}}{\text{K}}$$

As the temperature is lowered to 0 K, the entropy of the phase transition approaches zero:

$$\lim_{T \to 0} \Delta_r S = 0$$

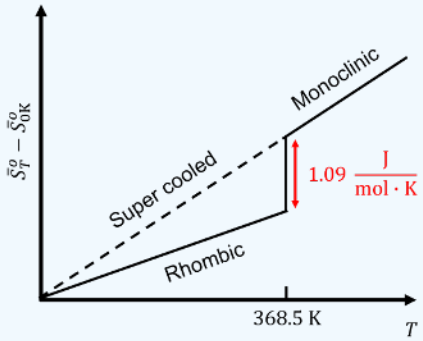


Figure 2.8.2: Schematic showing the entropy of the rhombic and monoclinic structures of sulfur as a function of temperature.

This shows that the entropy of the two crystalline forms are the same. The only way is if all species have the same absolute entropy at 0 K. For energy dispersal at 0 K:

1. Energy is as concentrated as it can be.
2. Only the very lowest energy states can be occupied.

For a pure, perfect crystalline solid at 0 K, there is only one energetic arrangement to represent its lowest energy state. We can use this to define a natural zero, giving entropy an absolute scale. The **third Law of Thermodynamics** states that the entropy of a pure substance in a perfect crystalline form is 0 $\frac{J}{mol \cdot K}$ at 0 K:

$$\bar{S}^{\circ}_{0\,\mathrm{K}} = 0$$

This is consistent with our molecular formula for entropy:

$$S = k \ln W$$

For a perfect crystal at 0 K, the number of ways the total energy of a system can be distributed is one ($W = 1$). The $\ln W$ term goes to zero, resulting in the perfect crystal at 0 K having zero entropy (Figure **2.8.3***a*).

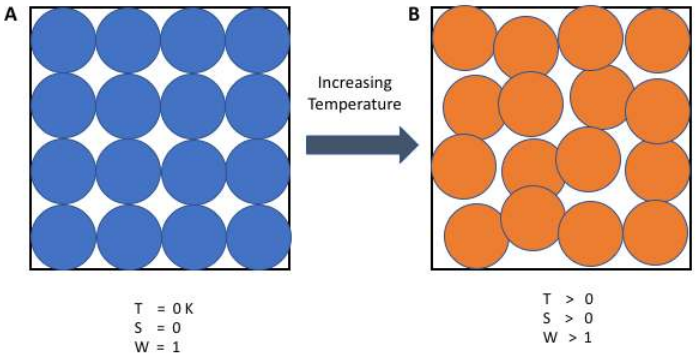


Figure **2.8.3**: (a) Single possible configuration for a system at absolute zero, i.e., only one microstate is accessible. Thus $S = k \ln W = 0$. (b) At temperatures greater than absolute zero, multiple microstates are accessible due to atomic dislocation (exaggerated in the figure). Since the number of accessible microstates is greater than 1, $S = k \ln W > 0$. (CC BY-SA 4.0; BlyumJ via Wikipedia)

It is certainly true that for the great majority of materials we end up with a crystalline material at sufficiently low materials (although there are odd exceptions like liquid helium). However, it should be mentioned that a completely *perfect* crystal can only be grown at zero Kelvin! It is not possible to grow anything at 0 K however. At any finite temperature the crystal always incorporates defects, more so if grown at higher temperatures. When cooled down very slowly the defects tend to be ejected from the lattice for the crystal to reach a new equilibrium with less defects. This tendency towards less and less disorder upon cooling is what the third law is all about.

However, the ordering process often becomes impossibly slow, certainly when approaching absolute zero. This means that real crystals always have *some* frozen in imperfections. Thus there is always *some* residual entropy. Fortunately, the effect is often too small to be measured. This is what allows us to ignore it in many cases (but not all). We could state the Third law of thermodynamics as follows:

Definition: Third law of thermodynamics

The entropy of a perfect crystal approaches zero when T approaches zero (but perfect crystals do not exist).

$$\lim_{T \to 0} S^{\circ}(T) = 0 \tag{2.8.1}$$

Another complication arises when the system undergoes a phase transition, e.g. the melting of ice. As we can write:

$$\Delta_{fus} H = q_P$$

If ice and water are in equilibrium with each other the process is quite reversible and so we have:

$$\Delta_{fus}S = \frac{q_{rev}}{T} = \frac{\Delta_{fus}H}{T}$$

This means that at the melting point the curve for S makes a sudden jump by this amount because all this happens at one an the same temperature. Entropies are typically calculated from calorimetric data (e.g., C_P measurements) and tabulated in standard molar form.

There are some clear trends in the entropy values of elements and molecules, e.g. when the noble gas gets heavier this induces more entropy. This is a direct consequence of the particle in the box formula. It has mass in the denominator and therefore the energy levels get more crowded together when m increases: more energy levels, more entropy.

> *The energy levels get more crowded together when m increases: more energy levels, more entropy*

There are tables for $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ as a function of temperature for numerous substances. As we discussed before the plimsoll defines are standard state in terms of pressure (1 bar) and of concentration reference states, if applicable, but temperature is the one of interest.

Residual Entropy in Carbon Monoxide

For most substances, the assumption made in Equation 2.8.1 regarding the Third Law is generally valid; however, there are notable exceptions, such as carbon monoxide. In its solid state, carbon monoxide molecules would ideally be fully ordered at absolute zero. However, due to the similar sizes of carbon and oxygen atoms and the molecule's weak dipole, it is possible for some molecules to be positioned "upside down"—with oxygen occupying a carbon site and vice versa (i.e., the C≡O and O≡C orientations are nearly isoenergetic in the lattice). When the crystal forms at higher temperatures, this disorder increases entropy, thereby lowering the Gibbs energy (G). Essentially, if each molecule can be placed into the lattice in two different orientations, the total number of possible configurations (W_{disorder}) for N molecules is 2^N.

This leads to an additional contribution to the entropy of

$$S_{disorder} = k \ln W_{disorder} = k \ln 2^N = Nk \ln 2 = 5.7\,\text{J/(mol K)}$$

At lower temperatures, the entropy term in $\Delta G = \Delta H - T\Delta S$ diminishes in significance, and the crystal should theoretically transition to a more ordered state with lower entropy. However, in practice, the kinetics of this process are extremely slow, preventing the ordering from occurring. As a result, solid CO retains **a nonzero entropy** even as it approaches absolute zero (Equation 2.8.1).

In principle *all* crystalline materials have this effect to some extent, but CO is unusual because the concentration of 'wrongly aligned' entities is of the order of 50% rather than say 1 in 10^{13} (a typical defect concentration in say single crystal silicon). The experimental residual entropy of CO is approximately 4.4 J/(mol K); this indicates that the two orientations of CO are not exactly identical in energy (i.e., equal probability of forming), which would give a residulate entropy of 5.7 J/(mol K).

Exercise 2.8.1

The entropy of a crystal composed of one mole of identical molecules is measured to be 9.134 J/K at 0 K. Determine the number of possible orientations each molecule can adopt within the crystal. Additionally, illustrate a molecule that would be expected to exhibit this behavior.

Summary

Residual entropy quantifies the remaining disorder or randomness in a system even at absolute zero temperature (0 K). According to the Third Law of Thermodynamics, the entropy of a perfect crystal approaches zero as the temperature nears absolute zero. However, some systems retain a nonzero entropy at 0 K, exhibiting residual entropy. This phenomenon represents an exception to the Third Law rather than a contradiction. The law assumes a perfect crystal with a singular, unique ground state, whereas systems with residual entropy, such as carbon monoxide, possess multiple degenerate ground states.

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2.9: Entropy Increases with Increasing Temperature

Learning Objectives

- Define entropy and its relation to energy flow.

Entropy versus temperature

We can put together the first and the second law for a reversible process with no other work than volume (PV) work and obtain:

$$dU = \delta q_{rev} + \delta w_{rev}$$

Entropy is the dispersal of energy and is related to heat:

$$\delta q_{rev} = TdS$$

Work is related to the change in volume:

$$\delta w_{rev} = -PdV$$

Plugging these into our expression for dU for reversible changes:

$$dU = TdS - PdV$$

We no longer have any path functions in the expression, as U, S and V are ***all state functions***. This means this expression must be an exact differential. We can generalize the expression to hold for irreversible processes, but then the expression becomes an inequality:

$$dU \leq TdS - PdV$$

This equality expresses U as a function of two variables, entropy and volume: $U(S,V)$. S and V are the ***natural variables*** of U.

Entropy and heat capacity

At constant volume, dU becomes:

$$dU = TdS$$

Recall that internal energy is related to constant volume heat capacity, C_V:

$$C_V = \left(\frac{dU}{dT}\right)_V$$

Combining these two expressions, we obtain:

$$dS = \frac{C_V}{T}dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T}dT$$

If we know how C_V changes with temperature, we can calculate the change in entropy, ΔS. Since heat capacity is always a positive value, entropy must increase as the temperature increases. There is nothing to stop us from expressing U in ***other*** variables, e.g. T and V. In fact, we can derive some interesting relationships if we do.

Example 21.1.1

1. Write U as a function of T and V.
2. Write U as a function of its natural variables.
3. Rearrange (2) to find an expression for dS.
4. Substitute (1) into (3) and rearrange. This is the definition of C_V.

5. Write out S as a function of T and V.

We can also derive an expression for the change in entropy as a function of constant pressure heat capacity, C_P. To start, we need to change from internal energy, U, to enthalpy, H:

$$\begin{aligned} H &= U + PV \\ dH &= dU + d(PV) \\ &= dU + PdV + VdP \end{aligned}$$

For reversible processes:

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS - PdV + PdV + VP \\ &= TdS + VdP \end{aligned}$$

The natural variables of the enthalpy are S and P (not: V). A similar derivation as above shows that the temperature change of entropy is related to the constant pressure heat capacity:

$$dH = TdS + VdP$$

At constant pressure:

$$dH = TdS + VdP$$

Recall that:

$$C_P = \frac{dH}{dT}$$

Combining, we obtain:

$$dS = \frac{C_P}{T} dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

This means that if we know the heat capacities as a function of temperature we can calculate how the entropy changes with temperature. Usually it is easier to obtain data under constant P conditions than for constant V, so that the route with C_p is the more common one.

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CHAPTER OVERVIEW

3: Free Energy and Thermodynamic Potentials

3.1: Total Differential of a Dependent Variable
3.2: Total Differential of the Internal Energy
3.3: Enthalpy, Helmholtz Energy, and Gibbs Energy
3.4: Closed Systems
3.5: Surface Work
3.6: Criteria for Spontaneity

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3.1: Total Differential of a Dependent Variable

Recall from Sec. 2.4.1 that the state of the system at each instant is defined by a certain minimum number of state functions, the independent variables. State functions not treated as independent variables are dependent variables. Infinitesimal changes in any of the independent variables will, in general, cause an infinitesimal change in each dependent variable.

A dependent variable is a function of the independent variables. The **total differential** of a dependent variable is an expression for the infinitesimal change of the variable in terms of the infinitesimal changes of the independent variables. As explained in Sec. F.2 of Appendix F, the expression can be written as a sum of terms, one for each independent variable. Each term is the product of a partial derivative with respect to one of the independent variables and the infinitesimal change of that independent variable. For example, if the system has two independent variables, and we take these to be T and V, the expression for the total differential of the pressure is

$$\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V \tag{5.1.1}$$

Thus, in the case of a fixed amount of an ideal gas with pressure given by $p = nRT/V$, the total differential of the pressure can be written

$$\mathrm{d}p = \frac{nR}{V}\,\mathrm{d}T - \frac{nRT}{V^2}\,\mathrm{d}V \tag{5.1.2}$$

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3.2: Total Differential of the Internal Energy

For a closed system undergoing processes in which the only kind of work is expansion work, the first law becomes $\mathrm{d}U = đq + đw = đq - p_\mathrm{b}\,\mathrm{d}V$. Since it will often be useful to make a distinction between expansion work and other kinds of work, this e-book will sometimes write the first law in the form

$$\mathrm{d}U = đq - p_\mathrm{b}\,\mathrm{d}V + đw' \qquad \begin{matrix}(5.2.1)\\(\text{closed system})\end{matrix}$$

where $đw'$ is **nonexpansion work**—that is, any thermodynamic work that is not expansion work.

Consider a closed system of one chemical component (e.g., a pure substance) in a single homogeneous phase. The only kind of work is expansion work, with V as the work variable. This kind of system has *two* independent variables (Sec. 2.4.3). During a *reversible* process in this system, the heat is $đq = T\,\mathrm{d}S$, the work is $đw = -p\,\mathrm{d}V$, and an infinitesimal internal energy change is given by

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \qquad \begin{matrix}(5.2.2)\\(\text{closed system, } C{=}1,\\ P{=}1,\ đw'{=}0)\end{matrix}$$

In the conditions of validity shown next to this equation, $C{=}1$ means there is one component (C is the number of components) and $P{=}1$ means there is one phase (P is the number of phases).

The appearance of the intensive variables T and p in Eq. 5.2.2 implies, of course, that the temperature and pressure are uniform throughout the system during the process. If they were not uniform, the phase would not be homogeneous and there would be more than two independent variables. The temperature and pressure are strictly uniform only if the process is reversible; it is not necessary to include "reversible" as one of the conditions of validity.

A real process approaches a reversible process in the limit of infinite slowness. For all practical purposes, therefore, we may apply Eq. 5.2.2 to a process obeying the conditions of validity and taking place so slowly that the temperature and pressure remain essentially uniform—that is, for a process in which the system stays very close to thermal and mechanical equilibrium.

Because the system under consideration has two independent variables, Eq. 5.2.2 is an expression for the total differential of U with S and V as the independent variables. In general, an expression for the differential $\mathrm{d}X$ of a state function X is a total differential if

1. Note that the work coordinate of any kind of dissipative work—work without a reversible limit—cannot appear in the expression for a total differential, because it is not a state function (Sec. 3.10).

   As explained in Appendix F, we may identify the coefficient of each term in an expression for the total differential of a state function as a partial derivative of the function. We identify the coefficients on the right side of Eq. 5.2.2 as follows:

   $$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad -p = \left(\frac{\partial U}{\partial V}\right)_S \qquad (5.2.3)$$

   The quantity given by the third partial derivative, $(\partial U/\partial n)_{S,V}$, is represented by the symbol μ (mu). This quantity is an intensive state function called the **chemical potential**.

   With these substitutions, Eq. 5.2.4 becomes

   $$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n \qquad \begin{matrix}(5.2.5)\\(\text{pure substance,}\\ P{=}1,\ đw'{=}0)\end{matrix}$$

   and this is a valid expression for the total differential of U under the given conditions.

   If a system contains a mixture of s different substances in a single phase, and the system is open so that the amount of each substance can vary independently, there are $2 + s$ independent variables and the total differential of U can be written

   $$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_{i=1}^{s} \mu_i\,\mathrm{d}n_i \qquad \begin{matrix}(5.2.6)\\(\text{open system,}\\ P{=}1,\ đw'{=}0)\end{matrix}$$

The coefficient μ_i is the chemical potential of substance i. We identify it as the partial derivative $(\partial U/\partial n_i)_{S,V,n_{j\neq i}}$.

> The term $-p\,\mathrm{d}V$ on the right side of Eq. 5.2.6 is the reversible work. However, the term $T\,\mathrm{d}S$ does not equal the reversible heat as it would if the system were closed. This is because the entropy change $\mathrm{d}S$ is partly due to the entropy of the matter transferred across the boundary. It follows that the remaining term, $\sum_i \mu_i\,\mathrm{d}n_i$ (sometimes called the "chemical work"), should not be interpreted as the energy brought into the system by the transfer of matter.

Suppose that in addition to expansion work, other kinds of reversible work are possible. Each work coordinate adds an additional independent variable. Thus, for a closed system of one component in one phase, with reversible nonexpansion work given by $đw' = Y\,\mathrm{d}X$, the total differential of U becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + Y\,\mathrm{d}X \qquad (5.2.7)$$
(closed system, C=1, P=1)

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3.3: Enthalpy, Helmholtz Energy, and Gibbs Energy

For the moment we shall confine our attention to closed systems with one component in one phase. The total differential of the internal energy in such a system is given by Eq. 5.2.2: $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$. The independent variables in this equation, S and V, are called the *natural variables* of U.

In the laboratory, entropy and volume may not be the most convenient variables to measure and control. Entropy is especially inconvenient, as its value cannot be measured directly. The way to change the independent variables is to make Legendre transforms, as explained in Sec. F.4 in Appendix F.

A Legendre transform of a dependent variable is made by subtracting one or more products of *conjugate variables*. In the total differential $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$, T and S are conjugates (that is, they comprise a *conjugate pair*), and $-p$ and V are conjugates. Thus the products that can be subtracted from U are either TS or $-pV$, or both. Three Legendre transforms of the internal energy are possible, defined as follows:

$$\textbf{Enthalpy} \qquad H \stackrel{\text{def}}{=} U + pV \tag{5.3.1}$$

$$\textbf{Helmholtz energy} \qquad A \stackrel{\text{def}}{=} U - TS \tag{5.3.2}$$

$$\textbf{Gibbs energy} \qquad G \stackrel{\text{def}}{=} U - TS + pV = H - TS \tag{5.3.3}$$

These definitions are used whether or not the system has only two independent variables.

The enthalpy, Helmholtz energy, and Gibbs energy are important functions used extensively in thermodynamics. They are state functions (because the quantities used to define them are state functions) and are extensive (because U, S, and V are extensive). If temperature or pressure are not uniform in the system, we can apply the definitions to constituent phases, or to subsystems small enough to be essentially uniform, and sum over the phases or subsystems.

> Alternative names for the Helmholtz energy are Helmholtz function, Helmholtz free energy, and work function. Alternative names for the Gibbs energy are Gibbs function and Gibbs free energy. Both the Helmholtz energy and Gibbs energy have been called simply free energy, and the symbol F has been used for both. The nomenclature in this e-book follows the recommendations of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007).

Expressions for infinitesimal changes of H, A, and G are obtained by applying the rules of differentiation to their defining equations:

$$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p \tag{5.3.4}$$

$$\mathrm{d}A = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T \tag{5.3.5}$$

$$\mathrm{d}G = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T + p\,\mathrm{d}V + V\,\mathrm{d}p \tag{5.3.6}$$

These expressions for $\mathrm{d}H$, $\mathrm{d}A$, and $\mathrm{d}G$ are general expressions for any system or phase with uniform T and p. They are *not* total differentials of H, A, and G, as the variables in the differentials in each expression are not independent.

A useful property of the enthalpy in a closed system can be found by replacing $\mathrm{d}U$ in Eq. 5.3.4 by the first law expression $đq - p\,\mathrm{d}V + đw'$, to obtain $\mathrm{d}H = đq + V\,\mathrm{d}p + đw'$. Thus, in a process at constant pressure ($\mathrm{d}p = 0$) with expansion work only ($đw' = 0$), we have

$$\mathrm{d}H = đq \qquad \text{(closed system, constant } p\text{, } đw' = 0\text{)} \tag{5.3.7}$$

The enthalpy change under these conditions is equal to the heat. The integrated form of this relation is $\int \mathrm{d}H = \int đq$, or

$$\Delta H = q \qquad \text{(closed system, constant } p\text{, } w' = 0\text{)} \tag{5.3.8}$$

Equation 5.3.7 is analogous to the following relation involving the internal energy, obtained from the first law:

$$\mathrm{d}U = đq \qquad (5.3.9)$$
(closed system, constant V, $đw' = 0$)

That is, in a process at constant volume with expansion work only, the internal energy change is equal to the heat.

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3.4: Closed Systems

In order to find expressions for the total differentials of H, A, and G in a closed system with one component in one phase, we must replace $\mathrm{d}U$ in Eqs. 5.3.4–5.3.6 with

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{5.4.1}$$

to obtain

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p \tag{5.4.2}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V \tag{5.4.3}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p \tag{5.4.4}$$

Equations 5.4.1–5.4.4 are sometimes called the **Gibbs equations**. They are expressions for the total differentials of the thermodynamic potentials U, H, A, and G in closed systems of one component in one phase with expansion work only. Each equation shows how the dependent variable on the left side varies as a function of changes in two independent variables (the natural variables of the dependent variable) on the right side.

By identifying the coefficients on the right side of Eqs. 5.4.1–5.4.4, we obtain the following relations (which again are valid for a closed system of one component in one phase with expansion work only):

from Eq. 5.4.1:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{5.4.5}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{5.4.6}$$

from Eq. 5.4.2:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{5.4.7}$$

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{5.4.8}$$

from Eq. 5.4.3:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.4.9}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{5.4.10}$$

from Eq. 5.4.4:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{5.4.11}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{5.4.12}$$

This e-book now uses for the first time an extremely useful mathematical tool called the **reciprocity relation** of a total differential (Sec. F.2). Suppose the independent variables are x and y and the total differential of a dependent state function f is given by

$$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y \tag{5.4.13}$$

where a and b are functions of x and y. Then the reciprocity relation is

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \tag{5.4.14}$$

The reciprocity relations obtained from the Gibbs equations (Eqs. 5.4.1–5.4.4) are called **Maxwell relations** (again valid for a closed system with $C=1$, $P=1$, and $đw'=0$):

from Eq. 5.4.1:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{5.4.15}$$

from Eq. 5.4.2:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{5.4.16}$$

from Eq. 5.4.3:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{5.4.17}$$

from Eq. 5.4.4:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \tag{5.4.18}$$

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3.5: Surface Work

Sometimes we need more than the usual two independent variables to describe an equilibrium state of a closed system of one substance in one phase. This is the case when, in addition to expansion work, another kind of work is possible. The total differential of U is then given by $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + Y\,\mathrm{d}X$ (Eq. 5.2.7), where $Y\,\mathrm{d}X$ represents the nonexpansion work $đw'$.

A good example of this situation is surface work in a system in which surface area is relevant to the description of the state.

A liquid–gas interface behaves somewhat like a stretched membrane. The upper and lower surfaces of the liquid film in the device depicted in Fig. 5.1 exert a force F on the sliding rod, tending to pull it in the direction that reduces the surface area. We can measure the force by determining the opposing force F_{ext} needed to prevent the rod from moving. This force is found to be proportional to the length of the rod and independent of the rod position x. The force also depends on the temperature and pressure.

The **surface tension** or interfacial tension, γ, is the force exerted by an interfacial surface per unit length. The film shown in Fig. 5.1 has two surfaces, so we have $\gamma = F/2l$ where l is the rod length.

To increase the surface area of the film by a practically-reversible process, we slowly pull the rod to the right in the $+x$ direction. The *system* is the liquid. The x component of the force exerted by the system on the surroundings at the moving boundary, F_x^{sys}, is equal to $-F$ (F is positive and F_x^{sys} is negative). The displacement of the rod results in surface work given by Eq. 3.1.2: $đw' = -F_x^{\text{sys}}\,\mathrm{d}x = 2\gamma l\,\mathrm{d}x$. The increase in surface area, $\mathrm{d}A_s$, is $2l\,\mathrm{d}x$, so the surface work is $đw' = \gamma\,\mathrm{d}A_s$ where γ is the work coefficient and A_s is the work coordinate. Equation 5.2.7 becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \gamma\,\mathrm{d}A_s \tag{5.7.1}$$

Substitution into Eq. 5.3.6 gives

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \gamma\,\mathrm{d}A_s \tag{5.7.2}$$

which is the total differential of G with T, p, and A_s as the independent variables. Identifying the coefficient of the last term on the right side as a partial derivative, we find the following expression for the surface tension:

$$\gamma = \left(\frac{\partial G}{\partial A_s}\right)_{T,p} \tag{5.7.3}$$

That is, the surface tension is not only a force per unit length, but also a Gibbs energy per unit area.

From Eq. 5.7.2, we obtain the reciprocity relation

$$\left(\frac{\partial \gamma}{\partial T}\right)_{p,A_s} = -\left(\frac{\partial S}{\partial A_s}\right)_{T,p} \tag{5.7.4}$$

It is valid to replace the partial derivative on the left side by $(\partial\gamma/\partial T)_p$ because γ is independent of A_s. Thus, the variation of surface tension with temperature tells us how the entropy of the liquid varies with surface area.

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3.6: Criteria for Spontaneity

In this section we combine the first and second laws in order to derive some general relations for changes during a reversible or irreversible process of a closed system. The temperature and pressure will be assumed to be practically uniform during the process, even if the process is irreversible. For example, the volume might be changing at a finite rate but very slowly, or there might be a spontaneous homogeneous reaction in a mixture of uniform temperature and pressure.

The second law states that $\mathrm{d}S$ is equal to $đq/T$ if the process is reversible, and is greater than $đq/T$ if the process is irreversible:

$$\mathrm{d}S \geq đq/T \qquad \begin{matrix}(5.8.1)\\ (^{\text{irrev}}_{\text{rev}}\text{, closed system})\end{matrix}$$

or

$$đq \leq T\,\mathrm{d}S \qquad \begin{matrix}(5.8.2)\\ (^{\text{irrev}}_{\text{rev}}\text{, closed system})\end{matrix}$$

The *inequalities* in these relations refer to an irreversible process and the *equalities* to a reversible process, as indicated by the notation $^{\text{irrev}}_{\text{rev}}$.

When we substitute $đq$ from Eq. 5.8.2 into the first law in the form $\mathrm{d}U = đq - p\,\mathrm{d}V + đw'$, where $đw'$ is nonexpansion work, we obtain the relation

$$\mathrm{d}U \leq T\,\mathrm{d}S - p\,\mathrm{d}V + đw' \qquad \begin{matrix}(5.8.3)\\ (^{\text{irrev}}_{\text{rev}}\text{, closed system})\end{matrix}$$

We substitute this relation for $\mathrm{d}U$ into the differentials of enthalpy, Helmholtz energy, and Gibbs energy given by Eqs. 5.3.4–5.3.6 to obtain three more relations:

$$\mathrm{d}H \leq T\,\mathrm{d}S + V\,\mathrm{d}p + đw' \qquad \begin{matrix}(5.8.4)\\ (^{\text{irrev}}_{\text{rev}}\text{, closed system})\end{matrix}$$

$$\mathrm{d}A \leq -S\,\mathrm{d}T - p\,\mathrm{d}V + đw' \qquad \begin{matrix}(5.8.5)\\ (^{\text{irrev}}_{\text{rev}}\text{, closed system})\end{matrix}$$

$$\mathrm{d}G \leq -S\,\mathrm{d}T + V\,\mathrm{d}p + đw' \qquad \begin{matrix}(5.8.6)\\ (^{\text{irrev}}_{\text{rev}}\text{, closed system})\end{matrix}$$

The last two of these relations provide valuable criteria for spontaneity under common laboratory conditions. Equation 5.8.5 shows that during a spontaneous irreversible change at constant temperature and volume, $\mathrm{d}A$ is less than $đw'$. If the only work is expansion work (i.e., $đw'$ is zero), the Helmholtz energy decreases during a spontaneous process at constant T and V and has its minimum value when the system reaches an equilibrium state.

Equation 5.8.6 is especially useful. From it, we can conclude the following:

- Ben-Amotz and Honig (*J. Chem. Phys.*, **118**, 5932–5936, 2003; *J. Chem. Educ.*, **83**, 132–137, 2006) developed a "rectification" procedure that simplifies the mathematical manipulation of inequalities. Following this procedure, we can write

  $$\mathrm{d}S = đq/T + đ\theta \qquad (5.8.7)$$

  where $đ\theta$ is an *excess entropy function* that is positive for an irreversible change and zero for a reversible change ($đ\theta \geq 0$). Solving for $đq$ gives the expression $đq = T\,\mathrm{d}S - T\,đ\theta$ that, when substituted in the first law expression $\mathrm{d}U = đq - p\,\mathrm{d}V + đw'$, produces

  $$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + đw' - T\,đ\theta \qquad (5.8.8)$$

  The equality of this equation is equivalent to the combined equality and inequality of Eq. 5.8.3. Then by substitution of this expression for $\mathrm{d}U$ into Eqs. 5.3.4–5.3.6, we obtain equalities equivalent to Eqs. 5.8.4–5.8.6, for example

  $$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + đw' - T\,đ\theta \qquad (5.8.9)$$

  Equation 5.8.9 tells us that during a process at constant T and p, with expansion work only ($đw'=0$), $\mathrm{d}G$ has the same sign as $-T\,đ\theta$: negative for an irreversible change and zero for a reversible change.

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CHAPTER OVERVIEW

4: Pure Substances

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4.3: U, H, and Cp in Closed Systems
4.4: Heating at Constant Volume or Pressure
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4.1: Volume Properties of Pure Substances

Two volume properties of a closed system are defined as follows:

$$\textbf{cubic expansion coefficient} \quad \alpha \stackrel{\text{def}}{=} \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{7.1.1}$$

$$\textbf{isothermal compressibility} \quad \kappa_T \stackrel{\text{def}}{=} -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{7.1.2}$$

The cubic expansion coefficient is also called the coefficient of thermal expansion and the expansivity coefficient. Other symbols for the isothermal compressibility are β and γ_T.

These definitions show that α is the fractional volume increase per unit temperature increase at constant pressure, and κ_T is the fractional volume decrease per unit pressure increase at constant temperature. Both quantities are *intensive* properties. Most substances have positive values of α, and all substances have positive values of κ_T, because a pressure increase at constant temperature requires a volume decrease.

The cubic expansion coefficient is not always positive. α is negative for liquid water below its temperature of maximum density, $3.98\,^\circ\text{C}$. The crystalline ceramics zirconium tungstate (ZrW_2O_8) and hafnium tungstate (HfW_2O_8) have the remarkable behavior of contracting uniformly and continuously in all three dimensions when they are heated from $0.3\,\text{K}$ to about $1050\,\text{K}$; α is negative throughout this very wide temperature range (T. A. Mary et al, *Science*, **272**, 90–92, 1996). The intermetallic compound YbGaGe has been found to have a value of α that is practically zero in the range $100–300\,\text{K}$ (James R. Salvador et al, *Nature*, **425**, 702–705, 2003).

If an amount n of a substance is in a single phase, we can divide the numerator and denominator of the right sides of Eqs. 7.1.1 and 7.1.2 by n to obtain the alternative expressions

$$\alpha = \frac{1}{V_\text{m}}\left(\frac{\partial V_\text{m}}{\partial T}\right)_p \tag{7.1.3}$$
(pure substance, P=1)

$$\kappa_T = -\frac{1}{V_\text{m}}\left(\frac{\partial V_\text{m}}{\partial p}\right)_T \tag{7.1.4}$$
(pure substance, P=1)

where V_m is the molar volume. P in the conditions of validity is the number of phases. Note that only intensive properties appear in Eqs. 7.1.3 and 7.1.4; the amount of the substance is irrelevant. Figures 7.1 and 7.2 show the temperature variation of α and κ_T for several substances.

If we choose T and p as the independent variables of the closed system, the total differential of V is given by

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p \tag{7.1.5}$$

With the substitutions $(\partial V/\partial T)_p = \alpha V$ (from Eq. 7.1.1) and $(\partial V/\partial p)_T = -\kappa_T V$ (from Eq. 7.1.2), the expression for the total differential of V becomes

$$\mathrm{d}V = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p \tag{7.1.6}$$
(closed system, C=1, P=1)

To find how p varies with T in a closed system kept at constant volume, we set $\mathrm{d}V$ equal to zero in Eq. 7.1.6: $0 = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p$, or $\mathrm{d}p/\mathrm{d}T = \alpha/\kappa_T$. Since $\mathrm{d}p/\mathrm{d}T$ under the condition of constant volume is the partial derivative $(\partial p/\partial T)_V$, we have the general relation

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T} \tag{7.1.7}$$
(closed system, C=1, P=1)

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4.2: Internal Pressure

The partial derivative $(\partial U/\partial V)_T$ applied to a fluid phase in a closed system is called the **internal pressure**. (Note that U and pV have dimensions of energy; therefore, U/V has dimensions of pressure.)

To relate the internal pressure to other properties, we divide Eq. 5.2.2 by $\mathrm{d}V$: $\mathrm{d}U/\mathrm{d}V = T(\mathrm{d}S/\mathrm{d}V) - p$. Then we impose a condition of constant T: $(\partial U/\partial V)_T = T(\partial S/\partial V)_T - p$. When we make a substitution for $(\partial S/\partial V)_T$ from the Maxwell relation of Eq. 5.4.17, we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (7.2.1)$$

(closed system, fluid phase, C=1)

This equation is sometimes called the "thermodynamic equation of state" of the fluid.

For an ideal-gas phase, we can write $p = nRT/V$ and then

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \frac{p}{T} \qquad (7.2.2)$$

Making this substitution in Eq. 7.2.1 gives us

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad (7.2.3)$$

(closed system of an ideal gas)

showing that the internal pressure of an ideal gas is zero.

> In Sec. 3.5.1, an ideal gas was defined as a gas (1) that obeys the ideal gas equation, and (2) for which U in a closed system depends only on T. Equation 7.2.3, derived from the first part of this definition, expresses the second part. It thus appears that the second part of the definition is redundant, and that we could define an ideal gas simply as a gas obeying the ideal gas equation. This argument is valid only if we assume the ideal-gas temperature is the same as the thermodynamic temperature (Secs. 2.3.5 and 4.3.4) since this assumption is required to derive Eq. 7.2.3. Without this assumption, we can't define an ideal gas solely by $pV = nRT$, where T is the ideal gas temperature.

Here is a simplified interpretation of the significance of the internal pressure. When the volume of a fluid increases, the average distance between molecules increases and the potential energy due to intermolecular forces changes. If attractive forces dominate, as they usually do unless the fluid is highly compressed, expansion causes the potential energy to *increase*. The internal energy is the sum of the potential energy and thermal energy. The internal pressure, $(\partial U/\partial V)_T$, is the rate at which the internal energy changes with volume at constant temperature. At constant temperature, the thermal energy is constant so that the internal pressure is the rate at which just the potential energy changes with volume. Thus, the internal pressure is a measure of the strength of the intermolecular forces and is positive if attractive forces dominate. (These attractive intermolecular forces are the cohesive forces that can allow a negative pressure to exist in a liquid; see Sec. 2.3.4.) In an ideal gas, intermolecular forces are absent and therefore the internal pressure of an ideal gas is zero.

With the substitution $(\partial p/\partial T)_V = \alpha/\kappa_T$ (Eq. 7.1.7), Eq. 7.2.1 becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T}{\kappa_T} - p \qquad (7.2.4)$$

(closed system, fluid phase, C=1)

The internal pressure of a liquid at $p = 1\,\mathrm{bar}$ is typically much larger than $1\,\mathrm{bar}$ (see Prob. 7.6). Equation 7.2.4 shows that, in this situation, the internal pressure is approximately equal to $\alpha T/\kappa_T$.

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4.3: U, H, and Cp in Closed Systems

For convenience in derivations to follow, expressions from Chap. 5 are repeated here that apply to processes in a closed system in the absence of nonexpansion work (i.e., đ $w' = 0$). For a process at constant volume we have [3]

$$\mathrm{d}U = \mathrm{d}q \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{4.3.1}$$

and for a process at constant pressure we have [4]

$$\mathrm{d}H = \mathrm{d}q \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{4.3.2}$$

A closed system of one component in a single phase has only two independent variables. In such a system, the partial derivatives above are complete and unambiguous definitions of C_V and C_p because they are expressed with two independent variables- T and V for C_V, and T and p for C_p. As mentioned on page 146, additional conditions would have to be specified to define C_V for a more complicated system; the same is true for C_p.

For a closed system of an ideal gas we have 5

$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T} \quad C_p = \frac{\mathrm{d}H}{\mathrm{d}T} \tag{4.3.3}$$

The relation between $C_{V,\,\mathrm{m}}$ and $C_{p,\,\mathrm{m}}$

The value of $C_{p,\,\mathrm{m}}$ for a substance is greater than $C_{V,\,\mathrm{m}}$. The derivation is simple in the case of a fixed amount of an ideal gas. Using substitutions from Eq. 7.3.3, we write

$$C_p - C_V = \frac{\mathrm{d}H}{\mathrm{d}T} - \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{\mathrm{d}(H-U)}{\mathrm{d}T} = \frac{\mathrm{d}(pV)}{\mathrm{d}T} = nR \tag{4.3.4}$$

Division by n to obtain molar quantities and rearrangement then gives

$$C_{p,\,\mathrm{m}} = C_{V,\,\mathrm{m}} + R \tag{4.3.5}$$

For any phase in general, we proceed as follows. First we write

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left[\frac{\partial (U+pV)}{\partial T}\right]_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{4.3.6}$$

Then we write the total differential of U with T and V as independent variables and identify one of the coefficients as C_V :

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = C_V\,\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V \tag{4.3.7}$$

When we divide both sides of the preceding equation by $\mathrm{d}T$ and impose a condition of constant p, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{4.3.8}$$

Substitution of this expression for $(\partial U/\partial T)_p$ in the equation for C_p yields

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{4.3.9}$$

Finally we set the partial derivative $(\partial U/\partial V)_T$ (the internal pressure) equal to $(\alpha T/\kappa_T) - p$ (Eq. 7.2.4) and $(\partial V/\partial T)_p$ equal to αV to obtain

$$C_p = C_V + \frac{\alpha^2 T V}{\kappa_T} \tag{4.3.10}$$

and divide by n to obtain molar quantities:

$$C_{p,\,\mathrm{m}} = C_{V,\,\mathrm{m}} + \frac{\alpha^2 T V_{\mathrm{m}}}{\kappa_T} \tag{4.3.11}$$

Since the quantity $\alpha^2 T V_{\mathrm{m}}/\kappa_T$ must be positive, $C_{p,\,\mathrm{m}}$ is greater than $C_{V,\,\mathrm{m}}$.

Typical values for heat capacities

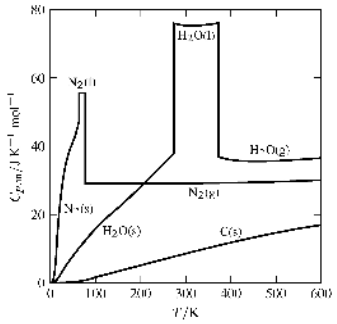


Figure 7.5 Temperature dependence of molar heat capacity at constant pressure ($p = 1$\br) of H_2O, N_2, and C(graphite).

Figure 7.5 shows the temperature dependence of \Cpm for several substances. The discontinuities seen at certain temperatures occur at equilibrium phase transitions. At these temperatures the heat capacity is in effect infinite, since the phase transition of a pure substance involves finite heat with zero temperature change.

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4.4: Heating at Constant Volume or Pressure

Consider the process of changing the temperature of a phase at constant volume.

> Keeping the volume exactly constant while increasing the temperature is not as simple as it may sound. Most solids expand when heated, unless we arrange to increase the external pressure at the same time. If we use solid walls to contain a fluid phase, the container volume will change with temperature. For practical purposes, these volume changes are usually negligible.

The rate of change of internal energy with T at constant V is the heat capacity at constant volume: $C_V = (\partial U/\partial T)_V$ (Eq. 7.3.1). Accordingly, an infinitesimal change of U is given by

$$\mathrm{d}U = C_V\,\mathrm{d}T \qquad (7.4.1)$$
(closed system, C=1, P=1, constant V)

and the finite change of U between temperatures T_1 and T_2 is

$$\Delta U = \int_{T_1}^{T_2} C_V\,\mathrm{d}T \qquad (7.4.2)$$
(closed system, C=1, P=1, constant V)

Three comments, relevant to these and other equations in this chapter, are in order:

1.
2. If, at a fixed volume and over the temperature range T_1 to T_2, the value of C_V is essentially constant (i.e., independent of T), Eq. 7.4.2 becomes

$$\Delta U = C_V(T_2 - T_1) \qquad (7.4.5)$$
(closed system, C=1, P=1, constant V and C_V)

An infinitesimal entropy change during a reversible process in a closed system is given according to the second law by $\mathrm{d}S = đq/T$. At constant volume, $đq$ is equal to $\mathrm{d}U$ which in turn equals $C_V\,\mathrm{d}T$. Therefore, the entropy change is

$$\mathrm{d}S = \frac{C_V}{T}\,\mathrm{d}T \qquad (7.4.6)$$
(closed system, C=1, P=1, constant V)

Integration yields the finite change

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T}\,\mathrm{d}T \qquad (7.4.7)$$
(closed system, C=1, P=1, constant V)

If C_V is treated as constant, Eq. 7.4.7 becomes

$$\Delta S = C_V \ln\frac{T_2}{T_1} \qquad (7.4.8)$$
(closed system, C=1, P=1, constant V and C_V)

(More general versions of the two preceding equations have already been given in Sec. 4.6.1.)

We may derive relations for a temperature change at constant *pressure* by the same methods. From $C_p = (\partial H/\partial T)_p$ (Eq. 7.3.2), we obtain

$$\Delta H = \int_{T_1}^{T_2} C_p\,\mathrm{d}T \qquad (7.4.9)$$
(closed system, C=1, P=1, constant p)

If C_p is treated as constant, Eq. 7.4.9 becomes

$$\Delta H = C_p(T_2 - T_1) \tag{7.4.10}$$
(closed system, C=1, P=1, constant p and C_p)

From $\mathrm{d}S = \mathrm{d}q/T$ and Eq. 7.3.2 we obtain for the entropy change at constant pressure

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T \tag{7.4.11}$$
(closed system, C=1, P=1, constant p)

Integration gives

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\,\mathrm{d}T \tag{7.4.12}$$
(closed system, C=1, P=1, constant p)

or, with C_p treated as constant,

$$\Delta S = C_p \ln \frac{T_2}{T_1} \tag{7.4.13}$$
(closed system, C=1, P=1, constant p and C_p)

C_p is positive, so heating a phase at constant pressure causes H and S to increase.

The Gibbs energy changes according to $(\partial G/\partial T)_p = -S$ (Eq. 5.4.11), so heating at constant pressure causes G to decrease.

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4.5: Partial Derivatives with Respect to T , p , and V

Tables of partial derivatives

The tables in this section collect useful expressions for partial derivatives of the eight state functions T, p, V, U, H, A, G, and S in a closed, single-phase system. Each derivative is taken with respect to one of the three easily-controlled variables T, p, or V while another of these variables is held constant. We have already seen some of these expressions, and the derivations of the others are indicated below.

We can use these partial derivatives (1) for writing an expression for the total differential of any of the eight quantities, and (2) for expressing the finite change in one of these quantities as an integral under conditions of constant T, p, or V. For instance, given the expressions

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\alpha V \tag{7.5.1}$$

we may write the total differential of S, taking T and p as the independent variables, as

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T - \alpha V\,\mathrm{d}p \tag{7.5.2}$$

Furthermore, the first expression is equivalent to the differential form

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T \tag{7.5.3}$$

provided p is constant; we can integrate this equation to obtain the finite change ΔS under isobaric conditions as shown in Eq. 7.4.12.

Both general expressions and expressions valid for an ideal gas are given in Tables 7.1, 7.2, and 7.3.

> We may derive the general expressions as follows. We are considering differentiation with respect only to T, p, and V. Expressions for $(\partial V/\partial T)_p$, $(\partial V/\partial p)_T$, and $(\partial p/\partial T)_V$ come from Eqs. 7.1.1, 7.1.2, and 7.1.7 and are shown as functions of α and κ_T. The reciprocal of each of these three expressions provides the expression for another partial derivative from the general relation
>
> $$(\partial y/\partial x)_z = \frac{1}{(\partial x/\partial y)_z} \tag{7.5.4}$$
>
> This procedure gives us expressions for the six partial derivatives of T, p, and V.
>
> The remaining expressions are for partial derivatives of U, H, A, G, and S. We obtain the expression for $(\partial U/\partial T)_V$ from Eq. 7.3.1, for $(\partial U/\partial V)_T$ from Eq. 7.2.4, for $(\partial H/\partial T)_p$ from Eq. 7.3.2, for $(\partial A/\partial T)_V$ from Eq. 5.4.9, for $(\partial A/\partial V)_T$ from Eq. 5.4.10, for $(\partial G/\partial p)_T$ from Eq. 5.4.12, for $(\partial G/\partial T)_p$ from Eq. 5.4.11, for $(\partial S/\partial T)_V$ from Eq. 7.4.6, for $(\partial S/\partial T)_p$ from Eq. 7.4.11, and for $(\partial S/\partial p)_T$ from Eq. 5.4.18.
>
> We can transform each of these partial derivatives, and others derived in later steps, to two other partial derivatives with the same variable held constant and the variable of differentiation changed. The transformation involves multiplying by an appropriate partial derivative of T, p, or V. For instance, from the partial derivative $(\partial U/\partial V)_T = (\alpha T/\kappa_T) - p$, we obtain
>
> $$\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\alpha T}{\kappa_T} - p\right)(-\kappa_T V) = (-\alpha T + \kappa_T p)\,V \tag{7.5.5}$$
>
> The remaining partial derivatives can be found by differentiating $U = H - pV$, $H = U + pV$, $A = U - TS$, and $G = H - TS$ and making appropriate substitutions. Whenever a partial derivative appears in a derived expression, it is replaced with an expression derived in an earlier step. The expressions derived by these steps constitute the full set shown in Tables 7.1, 7.2, and 7.3.
>
> Bridgman devised a simple method to obtain expressions for these and many other partial derivatives from a relatively small set of formulas (*Phys. Rev.*, **3**, 273–281, 1914; *The Thermodynamics of Electrical Phenomena in*

Metals and a Condensed Collection of Thermodynamic Formulas, Dover, New York, 1961, p. 199–241).

Example: Using Partial Derivatives to find the Joule–Thomson coefficient

The Joule–Thomson coefficient of a gas was defined in Eq. 6.3.3 by $\mu_{\mathrm{JT}} = (\partial T/\partial p)_H$. It can be evaluated with measurements of T and p during adiabatic throttling processes as described in Sec. 6.3.1.

To relate μ_{JT} to other properties of the gas, we write the total differential of the enthalpy of a closed, single-phase system in the form

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p \tag{7.5.6}$$

and divide both sides by $\mathrm{d}p$:

$$\frac{\mathrm{d}H}{\mathrm{d}p} = \left(\frac{\partial H}{\partial T}\right)_p \frac{\mathrm{d}T}{\mathrm{d}p} + \left(\frac{\partial H}{\partial p}\right)_T \tag{7.5.7}$$

Next we impose a condition of constant H; the ratio $\mathrm{d}T/\mathrm{d}p$ becomes a partial derivative:

$$0 = \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H + \left(\frac{\partial H}{\partial p}\right)_T \tag{7.5.8}$$

Rearrangement gives

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} \tag{7.5.9}$$

The left side of this equation is the Joule–Thomson coefficient. An expression for the partial derivative $(\partial H/\partial p)_T$ is given in Table 7.1, and the partial derivative $(\partial H/\partial T)_p$ is the heat capacity at constant pressure (Eq. 5.6.3). These substitutions give us the desired relation

$$\mu_{\mathrm{JT}} = \frac{(\alpha T - 1)V}{C_p} = \frac{(\alpha T - 1)V_{\mathrm{m}}}{C_{p,\mathrm{m}}} \tag{7.5.10}$$

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4.6: Standard States of Pure Substances

It is often useful to refer to a reference pressure, the **standard pressure**, denoted p°. The standard pressure has an arbitrary but constant value in any given application. Until 1982, chemists used a standard pressure of $1\,\text{atm}$ ($1.01325 \times 10^5\,\text{Pa}$). The IUPAC now recommends the value $p^\circ = 1\,\text{bar}$ (exactly $10^5\,\text{Pa}$). This e-book uses the latter value unless stated otherwise. (Note that there is no defined standard *temperature*.)

A superscript degree symbol ($^\circ$) denotes a standard quantity or standard-state conditions. An alternative symbol for this purpose, used extensively outside the U.S., is a superscript Plimsoll mark ($^\ominus$). (The Plimsoll mark is named after the British merchant Samuel Plimsoll, at whose instigation Parliament passed an act in 1875 requiring the symbol to be placed on the hulls of cargo ships to indicate the maximum depth for safe loading.)

A **standard state** of a pure substance is a particular reference state appropriate for the kind of phase and is described by intensive variables. This e-book follows the recommendations of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 61–62) for various standard states.

- Section 9.7 will introduce additional standard states for constituents of mixtures.

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4.7: Standard Molar Quantities of a Gas

A **standard molar quantity** of a substance is the molar quantity in the standard state at the temperature of interest. We have seen (Sec. 7.7) that the standard state of a pure *liquid* or *solid* is a real state, so any standard molar quantity of a pure liquid or solid is simply the molar quantity evaluated at the standard pressure and the temperature of interest.

The standard state of a *gas*, however, is a hypothetical state in which the gas behaves ideally at the standard pressure without influence of intermolecular forces. The properties of the gas in this standard state are those of an ideal gas. We would like to be able to relate molar properties of the real gas at a given temperature and pressure to the molar properties in the standard state at the same temperature.

We begin by using Eq. 7.8.7 to write an expression for the chemical potential of the real gas at pressure p':

$$\mu(p') = \mu^\circ(\mathrm{g}) + RT\ln\frac{f(p')}{p^\circ} = \mu^\circ(\mathrm{g}) + RT\ln\frac{p'}{p^\circ} + RT\ln\frac{f(p')}{p'} \tag{7.9.1}$$

We then substitute from Eq. 7.8.14 to obtain a relation between the chemical potential, the standard chemical potential, and measurable properties, all at the same temperature:

$$\mu(p') = \mu^\circ(\mathrm{g}) + RT\ln\frac{p'}{p^\circ} + \int_0^{p'}\left(V_\mathrm{m} - \frac{RT}{p}\right)\mathrm{d}p \qquad \begin{matrix}(7.9.2)\\(\textbf{pure gas})\end{matrix}$$

Note that this expression for μ is not what we would obtain by simply integrating $\mathrm{d}\mu = V_\mathrm{m}\,\mathrm{d}p$ from p° to p', because the real gas is not necessarily in its standard state of ideal-gas behavior at a pressure of $\mathbf{1\,bar}$.

Recall that the chemical potential μ of a pure substance is also its molar Gibbs energy $G_\mathrm{m} = G/n$. The standard chemical potential $\mu^\circ(\mathrm{g})$ of the gas is the standard molar Gibbs energy, $G^\circ_\mathrm{m}(\mathrm{g})$. Therefore Eq. 7.9.2 can be rewritten in the form

$$G_\mathrm{m}(p') = G^\circ_\mathrm{m}(\mathrm{g}) + RT\ln\frac{p'}{p^\circ} + \int_0^{p'}\left(V_\mathrm{m} - \frac{RT}{p}\right)\mathrm{d}p \tag{7.9.3}$$

The middle column of Table 7.5 contains an expression for $G_\mathrm{m}(p') - G^\circ_\mathrm{m}(\mathrm{g})$ taken from this equation. This expression contains all the information needed to find a relation between any other molar property and its standard molar value in terms of measurable properties. The way this can be done is as follows.

The relation between the chemical potential of a pure substance and its molar entropy is given by Eq. 7.8.3:

$$S_\mathrm{m} = -\left(\frac{\partial\mu}{\partial T}\right)_p \tag{7.9.4}$$

The standard molar entropy of the gas is found from Eq. 7.9.4 by changing μ to $\mu^\circ(\mathrm{g})$:

$$S^\circ_\mathrm{m}(\mathrm{g}) = -\left(\frac{\partial\mu^\circ(\mathrm{g})}{\partial T}\right)_p \tag{7.9.5}$$

By substituting the expression for μ given by Eq. 7.9.2 into Eq. 7.9.4 and comparing the result with Eq. 7.9.5, we obtain

$$S_\mathrm{m}(p') = S^\circ_\mathrm{m}(\mathrm{g}) - R\ln\frac{p'}{p^\circ} - \int_0^{p'}\left[\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p - \frac{R}{p}\right]\mathrm{d}p \tag{7.9.6}$$

The expression for $S_\mathrm{m} - S^\circ_\mathrm{m}(\mathrm{g})$ in the middle column of Table 7.5 comes from this equation. The equation, together with a value of S_m for a real gas obtained by the calorimetric method described in Sec. 6.2.1, can be used to evaluate $S^\circ_\mathrm{m}(\mathrm{g})$.

Now we can use the expressions for G_m and S_m to find expressions for molar quantities such as H_m and $C_{p,\mathrm{m}}$ relative to the respective standard molar quantities. The general procedure for a molar quantity X_m is to write an expression for X_m as a function of G_m and S_m and an analogous expression for $X^\circ_\mathrm{m}(\mathrm{g})$ as a function of $G^\circ_\mathrm{m}(\mathrm{g})$ and $S^\circ_\mathrm{m}(\mathrm{g})$. Substitutions for G_m and S_m from Eqs. 7.9.3 and 7.9.6 are then made in the expression for X_m, and the difference $X_\mathrm{m} - X^\circ_\mathrm{m}(\mathrm{g})$ taken.

For example, the expression for $U_\mathrm{m} - U^\circ_\mathrm{m}(\mathrm{g})$ in the middle column Table 7.5 was derived as follows. The equation defining the Gibbs energy, $G = U - TS + pV$, was divided by the amount n and rearranged to

$$U_{\mathrm{m}} = G_{\mathrm{m}} + TS_{\mathrm{m}} - pV_{\mathrm{m}} \tag{7.9.7}$$

The standard-state version of this relation is

$$U^{\circ}_{\mathrm{m}}(\mathrm{g}) = G^{\circ}_{\mathrm{m}}(\mathrm{g}) + TS^{\circ}_{\mathrm{m}}(\mathrm{g}) - p^{\circ}V^{\circ}_{\mathrm{m}}(\mathrm{g}) \tag{7.9.8}$$

where from the ideal gas law $p^{\circ}V^{\circ}_{\mathrm{m}}(\mathrm{g})$ can be replaced by RT. Substitutions from Eqs. 7.9.3 and 7.9.6 were made in Eq. 7.9.7 and the expression for $U^{\circ}_{\mathrm{m}}(\mathrm{g})$ in Eq. 7.9.8 was subtracted, resulting in the expression in the table.

For a real gas at low to moderate pressures, we can approximate V_{m} by $(RT/p) + B$ where B is the second virial coefficient (Eq. 7.8.17). Equation 7.9.2 then becomes

$$\mu \approx \mu^{\circ}(\mathrm{g}) + RT \ln \frac{p}{p^{\circ}} + Bp \tag{7.9.9}$$

The expressions in the last column of Table 7.5 use this equation of state. We can see what the expressions look like if the gas is ideal simply by setting B equal to zero. They show that when the pressure of an ideal gas increases at constant temperature, G_{m} and A_{m} increase, S_{m} decreases, and U_{m}, H_{m}, and $C_{p,\mathrm{m}}$ are unaffected.

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4.8: Phase Equilibria

Equilibrium conditions

If the state of an isolated system is an equilibrium state, this state does not change over time We expect an isolated system that is *not* in an equilibrium state to undergo a spontaneous, irreversible process and eventually to reach an equilibrium state. Just how rapidly this process occurs is a matter of kinetics, not thermodynamics. During this irreversible adiabatic process, the entropy increases until it reaches a maximum in the equilibrium state.

Simple derivation of equilibrium conditions

A system with two degrees of freedom is called *bivariant*, one with one degree of freedom is *univariant*, and one with no degrees of freedom is *invariant*. For a system of a pure substance, these three cases correspond to one, two, and three phases respectively. For instance, a system of liquid and gaseous H_2O (and no other substances) is univariant ($F = 3 - P = 3 - 2 = 1$); we are able to independently vary only one intensive property, such as T, while the liquid and gas remain in equilibrium.

Here is a simpler, less formal derivation of the three equilibrium conditions in a multiphase system of a single substance.

It is intuitively obvious that, unless there are special constraints (such as internal partitions), an equilibrium state must have thermal and mechanical equilibrium. A temperature difference between two phases would cause a spontaneous transfer of heat from the warmer to the cooler phase; a pressure difference would cause spontaneous flow of matter.

When some of the substance is transferred from one phase to another under conditions of constant T and p, the intensive properties of each phase remains the same including the chemical potential. The chemical potential of a pure phase is the Gibbs energy per amount of substance in the phase. We know that in a closed system of constant T and p with expansion work only, the total Gibbs energy decreases during a spontaneous process and is constant during a reversible process (Eq. 5.8.6). The Gibbs energy will decrease only if there is a transfer of substance from a phase of higher chemical potential to a phase of lower chemical potential, and this will be a spontaneous change. No spontaneous transfer is possible if both phases have the same chemical potential, so this is a condition for an equilibrium state.

The number of independent variables

From this point on, unless stated otherwise, the discussions of multiphase systems will implicitly assume the existence of thermal, mechanical, and transfer equilibrium. Equations will not explicitly show these equilibria as a condition of validity.

In the rest of this chapter, we shall assume the state of each phase can be described by the usual variables: temperature, pressure, and amount. That is, variables such as elevation in a gravitational field, interface surface area, and extent of stretching of a solid, are not relevant.

How many of the usual variables of an open multiphase one-substance equilibrium system are independent? To find out, we go through the following argument. In the absence of any kind of equilibrium, we could treat phase α as having the three independent variables T^α, p^α, and n^α, and likewise for every other phase. A system of P phases without thermal, mechanical, or transfer equilibrium would then have $3P$ independent variables.

> We must decide how to count the number of phases. It is usually of no thermodynamic significance whether a phase, with particular values of its intensive properties, is contiguous. For instance, splitting a crystal into several pieces is not usually considered to change the number of phases or the state of the system, provided the increased surface area makes no significant contribution to properties such as internal energy. Thus, the number of phases P refers to the number of different *kinds* of phases.

Each independent relation resulting from equilibrium imposes a restriction on the system and reduces the number of independent variables by one. A two-phase system with thermal equilibrium has the single relation $T^\beta = T^\alpha$. For a three-phase system, there are two such relations that are independent, for instance $T^\beta = T^\alpha$ and $T^\gamma = T^\alpha$. (The additional relation $T^\gamma = T^\beta$ is not independent since we may deduce it from the other two.) In general, thermal equilibrium gives $P - 1$ independent relations among temperatures.

By the same reasoning, mechanical equilibrium involves $P - 1$ independent relations among pressures, and transfer equilibrium involves $P - 1$ independent relations among chemical potentials.

The total number of independent relations for equilibrium is $3(P-1)$, which we subtract from $3P$ (the number of independent variables in the absence of equilibrium) to obtain the number of independent variables in the equilibrium system: $3P-3(P-1)=3$. Thus, *an open single-substance system with any number of phases has at equilibrium three independent variables*. For example, in equilibrium states of a two-phase system we may vary T, n^{α}, and n^{β} independently, in which case p is a dependent variable; for a given value of T, the value of p is the one that allows both phases to have the same chemical potential.

The Gibbs phase rule for a pure substance

The complete description of the state of a system must include the value of an *extensive* variable of each phase (e.g., the volume, mass, or amount) in order to specify how much of the phase is present. For an equilibrium system of P phases with a total of 3 independent variables, we may choose the remaining $3-P$ variables to be *intensive*. The number of these intensive independent variables is called the **number of degrees of freedom** or **variance**, F, of the system:

$$F=3-P \qquad \begin{matrix}(8.1.17)\\(\text{pure substance})\end{matrix}$$

> The application of the phase rule to multicomponent systems will be taken up in Sec. 13.1. Equation 8.1.17 is a special case, for $C=1$, of the more general Gibbs phase rule $F=C-P+2$.

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4.9: Phase Diagrams of Pure Substances

A **phase diagram** is a two-dimensional map showing which phase or phases are able to exist in an equilibrium state under given conditions. This chapter describes pressure–volume and pressure–temperature phase diagrams for a single substance, and Chap. 13 will describe numerous types of phase diagrams for multicomponent systems.

Features of phase diagrams

Two-dimensional phase diagrams for a single-substance system can be generated as projections of a three-dimensional surface in a coordinate system with Cartesian axes p, V/n, and T. A point on the three-dimensional surface corresponds to a physically-realizable combination of values, for an equilibrium state of the system containing a total amount n of the substance, of the variables p, V/n, and T.

The concepts needed to interpret single-substance phase diagrams will be illustrated with carbon dioxide.

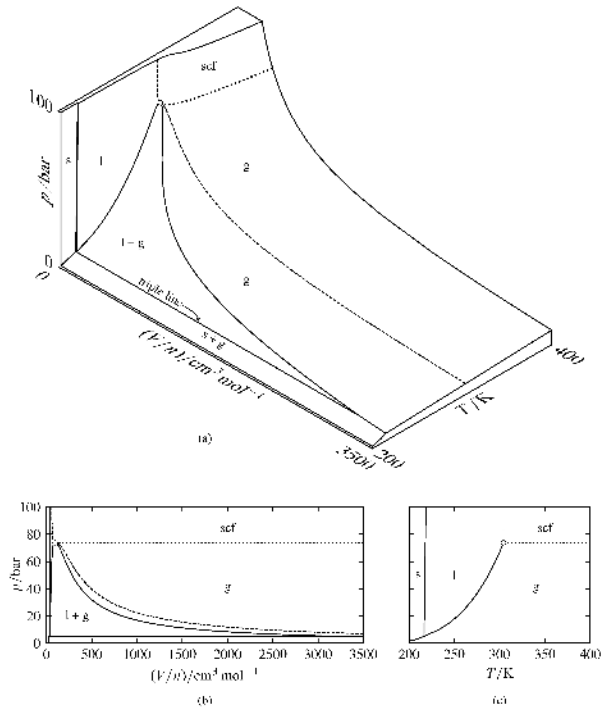


Figure 8.2 Relations among p, V/n, and T for carbon dioxide (based on data in *NIST Chemistry WebBook* and in S. Angus, B. Armstrong, and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State, Vol. 3, Carbon Dioxide*, Pergamon Press, Oxford, 1976). Areas are labeled with the stable phase or phases (scf stands for supercritical fluid). The open circle indicates the critical point.
(a) Three-dimensional p–(V/n)–T surface. The dashed curve is the critical isotherm at $T = 304.21\,\mathrm{K}$, and the dotted curve is a portion of the critical isobar at $p = 73.8\,\mathrm{bar}$.
(b) Pressure–volume phase diagram (projection of the surface onto the p –(V/n) plane).
(c) Pressure–temperature phase diagram (projection of the surface onto the p–T plane).

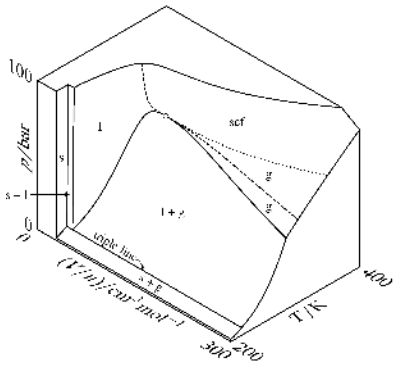


Figure 8.3 Three-dimensional p–(V/n)–T surface for CO_2, magnified along the V/n axis compared to Fig. 8.2. The open circle is the critical point, the dashed curve is the critical isotherm, and the dotted curve is a portion of the critical isobar.

Three-dimensional surfaces for carbon dioxide are shown at two different scales in Fig. 8.2 and in Fig. 8.3. In these figures, some areas of the surface are labeled with a single physical state: solid, liquid, gas, or supercritical fluid. A point in one of these areas corresponds to an equilibrium state of the system containing a single phase of the labeled physical state. The shape of the surface in this one-phase area gives the equation of state of the phase (i.e., the dependence of one of the variables on the other two). A point in an area labeled with two physical states corresponds to two coexisting phases. The **triple line** is the locus of points for all possible equilibrium systems of three coexisting phases, which in this case are solid, liquid, and gas. A point on the triple line can also correspond to just one or two phases.

The two-dimensional projections shown in Figs. 8.2(b) and 8.2(c) are pressure–volume and pressure–temperature phase diagrams. Because all phases of a multiphase equilibrium system have the same temperature and pressure (assuming there are no constraints such as internal adiabatic partitions), the projection of each two-phase area onto the pressure–temperature diagram is a curve, called a **coexistence curve** or **phase boundary**, and the projection of the triple line is a point, called a **triple point**.

How may we use a phase diagram? The two axes represent values of two independent variables, such as p and V/n or p and T. For given values of these variables, we place a point on the diagram at the intersection of the corresponding coordinates; this is the **system point**. Then depending on whether the system point falls in an area or on a coexistence curve, the diagram tells us the number and kinds of phases that can be present in the equilibrium system.

If the system point falls within an area labeled with the physical state of a *single* phase, only that one kind of phase can be present in the equilibrium system. A system containing a pure substance in a single phase is bivariant ($F = 3 - 1 = 2$), so we may vary two intensive properties independently. That is, the system point may move independently along two coordinates (p and V/n, or p and T) and still remain in the one-phase area of the phase diagram. When V and n refer to a single phase, the variable V/n is the molar volume V_m in the phase.

If the system point falls in an area of the pressure–volume phase diagram labeled with symbols for *two* phases, these two phases coexist in equilibrium. The phases have the same pressure and different molar volumes. To find the molar volumes of the individual phases, we draw a horizontal line of constant pressure, called a **tie line**, through the system point and extending from one edge of the area to the other. The horizontal position of each end of the tie line, where it terminates at the boundary with a one-phase area, gives the molar volume in that phase in the two-phase system. For an example of a tie line, see Fig. 8.9.

The triple line on the pressure–volume diagram represents the range of values of V/n in which three phases (solid, liquid, and gas) can coexist at equilibrium.

> Helium is the only substance lacking a solid–liquid–gas triple line. When a system containing the coexisting liquid and gas of ^{4}He is cooled to $2.17\,K$, a triple point is reached in which the third phase is a liquid called He-II, which has

the unique property of superfluidity. It is only at high pressures ($10\,\text{bar}$ or greater) that solid helium can exist.

A three-phase one-component system is invariant ($F = 3 - 3 = 0$); there is only one temperature (the triple-point temperature T_{tp}) and one pressure (the triple-point pressure p_{tp}) at which the three phases can coexist. The values of T_{tp} and p_{tp} are unique to each substance, and are shown by the position of the triple point on the pressure–temperature phase diagram. The molar volumes in the three coexisting phases are given by the values of V/n at the three points on the pressure–volume diagram where the triple line touches a one-phase area. These points are at the two ends and an intermediate position of the triple line. If the system point is at either end of the triple line, only the one phase of corresponding molar volume at temperature T_{tp} and pressure p_{tp} can be present. When the system point is on the triple line anywhere between the two ends, either two or three phases can be present. If the system point is at the position on the triple line corresponding to the phase of intermediate molar volume, there might be only that one phase present.

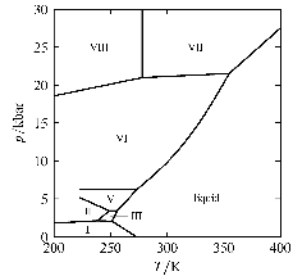


Figure 8.4 High-pressure pressure–temperature phase diagram of H_2O (based on data in D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, New York, 1969, Table 3.5, and Carl W. F. T. Pistorius et al, *J. Chem. Phys.*, **38**, 600–602, 1963). The roman numerals designate seven forms of ice.

At high pressures, a substance may have additional triple points for two solid phases and the liquid, or for three solid phases. This is illustrated by the pressure–temperature phase diagram of H_2O in Fig. 8.4, which extends to pressures up to $30\,\text{kbar}$. (On this scale, the liquid–gas coexistence curve lies too close to the horizontal axis to be visible.) The diagram shows seven different solid phases of H_2O differing in crystal structure and designated ice I, ice II, and so on. Ice I is the ordinary form of ice, stable below $2\,\text{bar}$. On the diagram are four triple points for two solids and the liquid and three triple points for three solids. Each triple point is invariant. Note how H_2O can exist as solid ice VI or ice VII above its standard melting point of $273\,\text{K}$ if the pressure is high enough ("hot ice").

Two-phase equilibrium

A system containing two phases of a pure substance in equilibrium is univariant. Both phases have the same values of T and of p, but these values are not independent because of the requirement that the phases have equal chemical potentials. We may vary only one intensive variable of a pure substance (such as T or p) independently while two phases coexist in equilibrium.

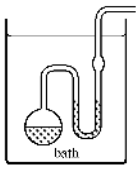


Figure 8.5 An isoteniscope. The liquid to be investigated is placed in the vessel and U-tube, as indicated by shading, and maintained at a fixed temperature in the bath. The pressure in the side tube is reduced until the liquid boils gently and its vapor sweeps out the air. The pressure is adjusted until the liquid level is the same in both limbs of the U-tube; the vapor pressure of the liquid is then equal to the pressure in the side tube, which can be measured with a manometer.

At a given temperature, the pressure at which solid and gas or liquid and gas are in equilibrium is called the **vapor pressure** or **saturation vapor pressure** of the solid or liquid. The vapor pressure of a solid is sometimes called the **sublimation pressure**. We may measure the vapor pressure of a liquid at a fixed temperature with a simple device called an isoteniscope (Fig. 8.5).

> In a system of more than one substance, *vapor pressure* can refer to the partial pressure of a substance in a gas mixture equilibrated with a solid or liquid of that substance. The effect of total pressure on vapor pressure will be discussed in Sec. 12.8.1. This e-book refers to the *saturation* vapor pressure of a liquid when it is necessary to indicate that it is the pure liquid and pure gas phases that are in equilibrium at the same pressure.

At a given pressure, the **melting point** or **freezing point** is the temperature at which solid and liquid are in equilibrium, the **boiling point** or **saturation temperature** is the temperature at which liquid and gas are in equilibrium, and the **sublimation temperature** or **sublimation point** is the temperature at which solid and gas are in equilibrium.

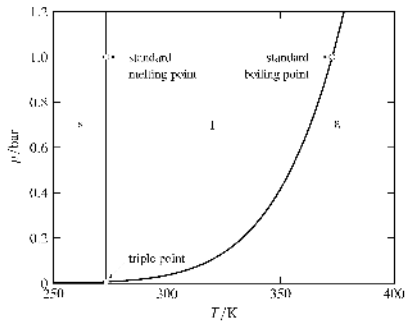


Figure 8.6 Pressure–temperature phase diagram of H_2O. (Based on data in *NIST Chemistry WebBook*.)

The relation between temperature and pressure in a system with two phases in equilibrium is shown by the coexistence curve separating the two one-phase areas on the pressure–temperature diagram (see Fig. 8.6). Consider the liquid–gas curve. If we think of T as the independent variable, the curve is a **vapor-pressure curve** showing how the vapor pressure of the liquid varies with temperature. If, however, p is the independent variable, then the curve is a **boiling-point curve** showing the dependence of the boiling point on pressure.

The *normal* melting point or boiling point refers to a pressure of one atmosphere, and the *standard* melting point or boiling point refers to the standard pressure. Thus, the normal boiling point of water ($99.97\,°C$) is the boiling point at $1\,atm$; this temperature is also known as the *steam point*. The standard boiling point of water ($99.61\,°C$) is the boiling point at the slightly lower pressure of $1\,bar$.

Coexistence curves will be discussed further in Sec. 8.4.

The critical point

Every substance has a certain temperature, the **critical temperature**, above which only one fluid phase can exist at any volume and pressure (Sec. 2.2.3). The **critical point** is the point on a phase diagram corresponding to liquid–gas coexistence at the critical temperature, and the **critical pressure** is the pressure at this point.

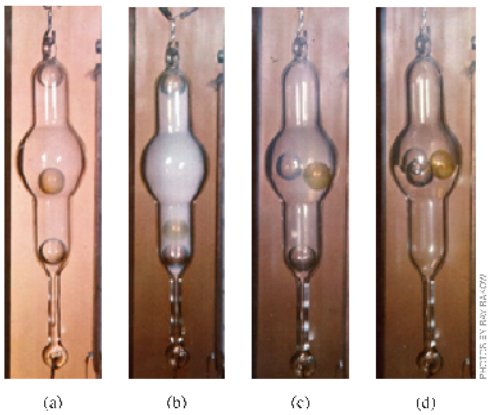


Figure 8.7 Glass bulb filled with CO_2 at a value of V/n close to the critical value, viewed at four different temperatures. The three balls have densities less than, approximately equal to, and greater than the critical density. (Photos by permission of the photographer; they appeared in Jan V. Sengers and Anneke Levelt Sengers, *Chem. Eng. News*, June 10, 104–118, 1968.)
(a) Supercritical fluid at a temperature above the critical temperature.
(b) Intense opalescence just above the critical temperature.
(c) Meniscus formation slightly below the critical temperature; liquid and gas of nearly the same density.
(d) Temperature well below the critical temperature; liquid and gas of greatly different densities.

To observe the critical point of a substance experimentally, we can evacuate a glass vessel, introduce an amount of the substance such that V/n is approximately equal to the molar volume at the critical point, seal the vessel, and raise the temperature above the critical temperature. The vessel now contains a single fluid phase. When the substance is slowly cooled to a temperature slightly above the critical temperature, it exhibits a cloudy appearance, a phenomenon called *critical opalescence* (Fig. 8.7). The opalescence is the scattering of light caused by large local density fluctuations. At the critical temperature, a meniscus forms between liquid and gas phases of practically the same density. With further cooling, the density of the liquid increases and the density of the gas decreases.

At temperatures above the critical temperature and pressures above the critical pressure, the one existing fluid phase is called a **supercritical fluid**. Thus, a supercritical fluid of a pure substance is a fluid that does not undergo a phase transition to a different fluid phase when we change the pressure at constant temperature or change the temperature at constant pressure.

If, however, we increase p at constant T, the supercritical fluid will change to a solid. In the phase diagram of H_2O, the coexistence curve for ice VII and liquid shown in Fig. 8.4 extends to a higher temperature than the critical temperature of $647\,K$. Thus, supercritical water can be converted to ice VII by isothermal compression.

A fluid in the supercritical region can have a density comparable to that of the liquid, and can be more compressible than the liquid. Under supercritical conditions, a substance is often an excellent solvent for solids and liquids. By varying the pressure or

temperature, the solvating power can be changed; by reducing the pressure isothermally, the substance can be easily removed as a gas from dissolved solutes. These properties make supercritical fluids useful for chromatography and solvent extraction.

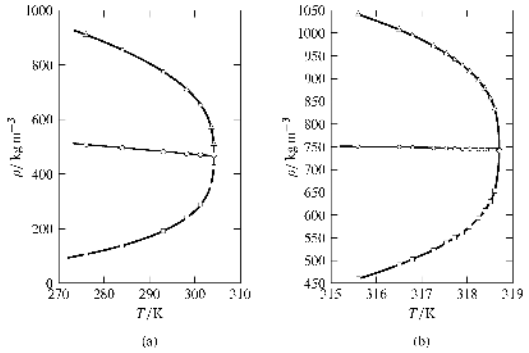


Figure 8.8 Densities of coexisting gas and liquid phases close to the critical point as functions of temperature for (a) CO_2 (based on data in A. Michels, B. Blaisse, and C. Michels, *Proc. R. Soc. London, Ser. A*, **160**, 358–375, 1937); (b) SF_6 (data of M. W. Pestak et al, *Phys. Rev. B*, **36**, 599–614, 1987, Table VII). Experimental gas densities are shown by open squares and experimental liquid densities by open triangles. The mean density at each experimental temperature is shown by an open circle. The open diamond is at the critical temperature and critical density.

The critical temperature of a substance can be measured quite accurately by observing the appearance or disappearance of a liquid–gas meniscus, and the critical pressure can be measured at this temperature with a high-pressure manometer. To evaluate the density at the critical point, it is best to extrapolate the mean density of the coexisting liquid and gas phases, $(\rho^l + \rho^g)/2$, to the critical temperature as illustrated in Fig. 8.8. The observation that the mean density closely approximates a linear function of temperature, as shown in the figure, is known as the **law of rectilinear diameters**, or the law of Cailletet and Matthias. This law is an approximation, as can be seen by the small deviation of the mean density of SF_6 from a linear relation very close to the critical point in Fig. 8.8(b). This failure of the law of rectilinear diameters is predicted by recent theoretical treatments (Jingtao Wang and Mikhail A. Anisimov, *Phys. Rev. E*, **75**, 051107, 2007; Hassan Behnejad, Jan V. Sengers, and Mikhail A. Anisimov, in A. R. H. Goodwin, J. V. Sengers, and C. J. Peters, editors, *Applied Thermodynamics of Fluids*, pages 321–367, Royal Society of Chemistry, Cambridge, 2010).

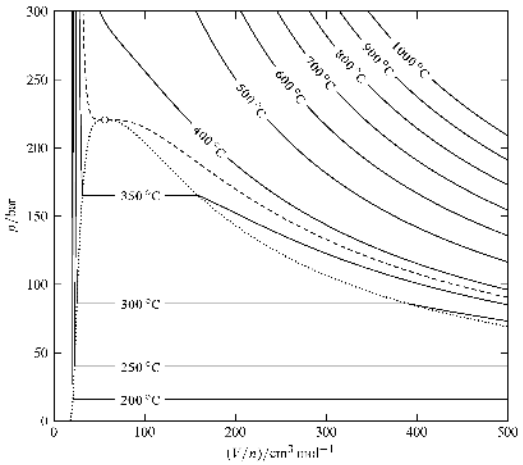


Figure 8.10 Isotherms for the fluid phases of H_2O (based on data in *NIST Chemistry WebBook*). The open circle indicates the critical point, the dashed curve is the critical isotherm at **373.95 °C**, and the dotted curve encloses the two-phase area of the pressure–volume phase diagram. The triple line lies too close to the bottom of the diagram to be visible on this scale.

Figure 8.10 is a pressure–volume phase diagram for H_2O. On the diagram are drawn *isotherms* (curves of constant T). These isotherms define the shape of the three-dimensional p–(V/n)–T surface. The area containing the horizontal isotherm segments is the two-phase area for coexisting liquid and gas phases. The boundary of this area is defined by the dotted curve drawn through the ends of the horizontal segments. The one-phase liquid area lies to the left of this curve, the one-phase gas area lies to the right, and the critical point lies at the top.

The diagram contains the information needed to evaluate the molar volume at any temperature and pressure in the one-phase region and the derivatives of the molar volume with respect to temperature and pressure. At a system point in the one-phase region, the slope of the isotherm passing through the point is the partial derivative $(\partial p/\partial V_m)_T$. Since the isothermal compressibility is given by $\kappa_T = -(1/V_m)(\partial V_m/\partial p)_T$, we have

$$\kappa_T = -\frac{1}{V_m \times \text{slope of isotherm}} \tag{8.2.9}$$

We see from Fig. 8.10 that the slopes of the isotherms are large and negative in the liquid region, smaller and negative in the gas and supercritical fluid regions, and approach zero at the critical point. Accordingly, the isothermal compressibility of the gas and the supercritical fluid is much greater than that of the liquid, approaching infinity at the critical point. The critical opalescence seen in Fig. 8.7 is caused by local density fluctuations, which are large when κ_T is large.

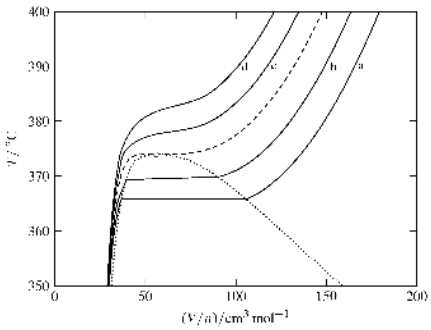


Figure 8.11 Isobars for H_2O (based on data in *NIST Chemistry WebBook*). The open circle indicates the critical point, the dashed curve is the critical isobar at **220.64 bar**, and the dotted curve encloses the two-phase area of the temperature–volume phase diagram. Solid curves: a, $p = 200\,\text{bar}$; b, $p = 210\,\text{bar}$; c, $p = 230\,\text{bar}$; d, $p = 240\,\text{bar}$.

Figure 8.11 shows isobars for H_2O instead of isotherms. At a system point in the one-phase region, the slope of the isobar passing through the point is the partial derivative $(\partial T/\partial V_m)_p$. The cubic expansion coefficient α is equal to $(1/V_m)(\partial V_m/\partial T)_p$, so we have

$$\alpha = \frac{1}{V_m \times \text{slope of isobar}} \tag{8.2.10}$$

The figure shows that the slopes of the isobars are large and positive in the liquid region, smaller and negative in the gas and supercritical fluid regions, and approach zero at the critical point. Thus the gas and the supercritical fluid have much larger cubic expansion coefficients than the liquid. The value of α approaches infinity at the critical point, meaning that in the critical region the density distribution is greatly affected by temperature gradients. This may account for the low position of the middle ball in Fig. 8.7(b).

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CHAPTER OVERVIEW

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5.1: Composition Variables

A **composition variable** is an intensive property that indicates the relative amount of a particular species or substance in a phase.

Species and substances

We sometimes need to make a distinction between a species and a substance. A **species** is any entity of definite elemental composition and charge and can be described by a chemical formula, such as H_2O, H_3O^+, NaCl, or Na^+. A **substance** is a species that can be prepared in a pure state (e.g., N_2 and NaCl). Since we cannot prepare a macroscopic amount of a single kind of ion by itself, a charged species such as H_3O^+ or Na^+ is not a substance. Chap. 10 will discuss the special features of mixtures containing charged species.

Mixtures in general

The **mole fraction** of species i is defined by

$$x_i \stackrel{\text{def}}{=} \frac{n_i}{\sum_j n_j} \quad \text{or} \quad y_i \stackrel{\text{def}}{=} \frac{n_i}{\sum_j n_j} \qquad \begin{matrix}(9.1.1)\\(P{=}1)\end{matrix}$$

where n_i is the amount of species i and the sum is taken over all species in the mixture. The symbol x_i is used for a mixture in general, and y_i is used when the mixture is a gas.

The **mass fraction**, or weight fraction, of species i is defined by

$$w_i \stackrel{\text{def}}{=} \frac{m(i)}{m} = \frac{n_i M_i}{\sum_j n_j M_j} \qquad \begin{matrix}(9.1.2)\\(P{=}1)\end{matrix}$$

where $m(i)$ is the mass of species i and m is the total mass.

The **concentration**, or molarity, of species i in a mixture is defined by

$$c_i \stackrel{\text{def}}{=} \frac{n_i}{V} \qquad \begin{matrix}(9.1.3)\\(P{=}1)\end{matrix}$$

The symbol M is often used to stand for units of mol L^{-1}, or mol dm^{-3}. Thus, a concentration of $0.5\,\mathrm{M}$ is 0.5 moles per liter, or 0.5 molar.

> Concentration is sometimes called “amount concentration” or “molar concentration” to avoid confusion with number concentration (the number of *particles* per unit volume). An alternative notation for c_A is [A].

A **binary mixture** is a mixture of *two* substances.

Solutions

A **solution**, strictly speaking, is a mixture in which one substance, the **solvent**, is treated in a special way. Each of the other species comprising the mixture is then a **solute**. The solvent is denoted by A and the solute species by B, C, and so on. (Some chemists denote the solvent by subscript 1 and use 2, 3, and so on for solutes.) Although in principle a solution can be a gas mixture, in this section we will consider only liquid and solid solutions.

We can prepare a solution of varying composition by gradually mixing one or more solutes with the solvent so as to continuously increase the solute mole fractions. During this mixing process, the physical state (liquid or solid) of the solution remains the same as that of the pure solvent. When the sum of the solute mole fractions is small compared to x_A (i.e., x_A is close to unity), the solution is called *dilute*. As the solute mole fractions increase, we say the solution becomes more *concentrated*.

Mole fraction, mass fraction, and concentration can be used as composition variables for both solvent and solute, just as they are for mixtures in general. A fourth composition variable, molality, is often used for a solute. The **molality** of solute species B is defined by

$$m_\mathrm{B} \stackrel{\text{def}}{=} \frac{n_\mathrm{B}}{m(\mathrm{A})} \qquad \begin{matrix}(9.1.4)\\(\text{solution})\end{matrix}$$

where $m(\mathrm{A}) = n_\mathrm{A} M_\mathrm{A}$ is the mass of solvent. The symbol m is sometimes used to stand for units of mol kg^{-1}, although this should be discouraged because m is also the symbol for meter. For example, a solute molality of $0.6\,\mathrm{m}$ is 0.6 moles of solute per kilogram of solvent, or 0.6 molal.

The composition of a mixture

We can describe the composition of a phase with the amounts of each species, or with any of the composition variables defined earlier: mole fraction, mass fraction, concentration, or molality. If we use mole fractions or mass fractions to describe the composition, we need the values for all but one of the species, since the sum of all fractions is unity.

Other composition variables are sometimes used, such as volume fraction, mole ratio, and mole percent. To describe the composition of a gas mixture, partial pressures can be used (Sec. 9.3.1).

When the composition of a mixture is said to be *fixed* or *constant* during changes of temperature, pressure, or volume, this means there is no change in the relative *amounts* or *masses* of the various species. A mixture of fixed composition has fixed values of mole fractions, mass fractions, and molalities, but not necessarily of concentrations and partial pressures. Concentrations will change if the volume changes, and partial pressures in a gas mixture will change if the pressure changes.

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5.2: Partial Molar Quantities

The symbol X_i, where X is an extensive property of a homogeneous mixture and the subscript i identifies a constituent species of the mixture, denotes the **partial molar quantity** of species i defined by

$$X_i \overset{\text{def}}{=} \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad \begin{matrix}(9.2.1)\\(\textbf{mixture})\end{matrix}$$

This is the rate at which property X changes with the amount of species i added to the mixture as the temperature, the pressure, and the amounts of all other species are kept constant. A partial molar quantity is an *intensive* state function. Its value depends on the temperature, pressure, and composition of the mixture.

Keep in mind that as a practical matter, a macroscopic amount of a charged species (i.e., an ion) cannot be added by itself to a phase because of the huge electric charge that would result. Thus if species i is charged, X_i as defined by Eq. 9.2.1 is a theoretical concept whose value cannot be determined experimentally.

> An older notation for a partial molar quantity uses an overbar: $\overline{X}_i$. The notation X_i' was suggested in the first edition of the IUPAC Green Book (Ian Mills et al, *Quantities, Units and Symbols in Physical Chemistry*, Blackwell, Oxford, 1988, p. 44), but is not mentioned in later editions.

Example 5.2.1

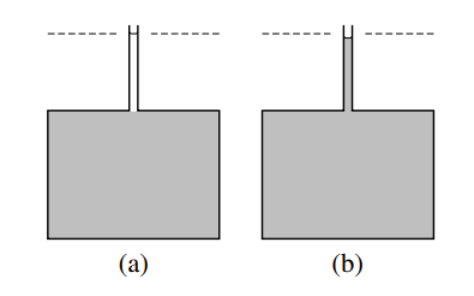


Figure **5.2.1**: Addition of pure methanol (substance B) to a water-methanol mixture at constant T and p.

(a) $40.75\ \text{cm}^3$ (one mole) of methanol is placed in a narrow tube above a much greater volume of a mixture (shaded) of composition $x_\text{B} = 0.307$. The dashed line indicates the level of the upper meniscus.

(b) After the two liquid phases have mixed by diffusion, the volume of the mixture has increased by only $38.8\ \text{cm}^3$.

Partial molar volume

In order to gain insight into the significance of a partial molar quantity as defined by Eq. 9.2.1, let us first apply the concept to the *volume* of an open single-phase system. Volume has the advantage for our example of being an extensive property that is easily visualized. Let the system be a binary mixture of water (substance A) and methanol (substance B), two liquids that mix in all proportions. The partial molar volume of the methanol, then, is the rate at which the system volume changes with the amount of methanol added to the mixture at constant temperature and pressure: $V_\text{B} = (\partial V/\partial n_\text{B})_{T,p,n_\text{A}}$.

At $25\,^\circ\text{C}$ and $1\ \text{bar}$, the molar volume of pure water is $V^*_{\text{m,A}} = 18.07\,\text{cm}^3\ \text{mol}^{-1}$ and that of pure methanol is $V^*_{\text{m,B}} = 40.75\,\text{cm}^3\ \text{mol}^{-1}$. If we mix $100.0\,\text{cm}^3$ of water at $25\,^\circ\text{C}$ with $100.0\,\text{cm}^3$ of methanol at $25\,^\circ\text{C}$, we find the volume of the resulting mixture at $25\,^\circ\text{C}$ is not the sum of the separate volumes, $200.0\,\text{cm}^3$, but rather the slightly smaller value $193.1\,\text{cm}^3$. The difference is due to new intermolecular interactions in the mixture compared to the pure liquids.

Let us calculate the mole fraction composition of this mixture:

$$n_\text{A} = \frac{V^*_\text{A}}{V^*_{\text{m,A}}} = \frac{100.0\,\text{cm}^3}{18.07\,\text{cm}^3\ \text{mol}^{-1}} = 5.53\,\text{mol} \qquad (9.2.2)$$

$$n_B = \frac{V_B^*}{V_{m,B}^*} = \frac{100.0\,cm^3}{40.75\,cm^3\ mol^{-1}} = 2.45\,mol \tag{9.2.3}$$

$$x_B = \frac{n_B}{n_A + n_B} = \frac{2.45\,mol}{5.53\,mol + 2.45\,mol} = 0.307 \tag{9.2.4}$$

Now suppose we prepare a large volume of a mixture of this composition ($x_B = 0.307$) and add an additional $40.75\ cm^3$ (one mole) of pure methanol, as shown in Fig. 9.1(a). If the initial volume of the mixture at $25°C$ was $10,000.0\ cm^3$, we find the volume of the new mixture at the same temperature is $10,038.8\ cm^3$, an increase of $38.8\ cm^3$ - see Fig. 9.1(b). The amount of methanol added is not infinitesimal, but it is small enough compared to the amount of initial mixture to cause very little change in the mixture composition: x_B

increases by only 0.5%. Treating the mixture as an open system, we see that the addition of one mole of methanol to the system at constant T, p, and n_A causes the system volume to increase by $38.8\ cm^3$. To a good approximation, then, the partial molar volume of methanol in the mixture, $V_B = (\partial V/\partial n_B)_{T,p,n_A}$, is given by $\Delta V/\Delta n_B = 38.8\ cm^3\ mol^{-1}$.

The volume of the mixture to which we add the methanol does not matter as long as it is large. We would have observed practically the same volume increase, $38.8\ cm^3$, if we had mixed one mole of pure methanol with $100,000.0\ cm^3$ of the mixture instead of only $10,000.0\ cm^3$.

Thus, we may interpret the partial molar volume of B as the volume change per amount of B added at constant T and p when B is mixed with such a large volume of mixture that the composition is not appreciably affected. We may also interpret the partial molar volume as the volume change per amount when an infinitesimal amount is mixed with a finite volume of mixture.

The partial molar volume of B is an intensive property that is a function of the composition of the mixture, as well as of T and p. The limiting value of V_B as x_B approaches 1 (pure B) is $V_{m,B}^*$, the molar volume of pure B. We can see this by writing $V = n_B V_{m,B}^*$ for pure B, giving us $V_B\,(x_B = 1) = \left(\partial n_B V_{m,B}^*/\partial n_B\right)_{T,p,n_A} = V_{m,B}^*$.

If the mixture is a binary mixture of A and B, and x_B is small, we may treat the mixture as a dilute solution of solvent A and solute B. As x_B approaches 0 in this solution, V_B approaches a certain limiting value that is the volume increase per amount of B mixed with a large amount of pure A. In the resulting mixture, each solute molecule is surrounded only by solvent molecules. We denote this limiting value of V_B by V_B^∞, the partial molar volume of solute B at infinite dilution.
It is possible for a partial molar volume to be negative. Magnesium sulfate, in aqueous solutions of molality less than $0.07\ mol\ kg^{-1}$, has a negative partial molar volume. Physically, this means that when a small amount of crystalline $MgSO_4$ dissolves at constant temperature in water, the liquid phase contracts. This unusual behavior is due to strong attractive water-ion interactions.

The total differential of the volume in an open system

Consider an open single-phase system consisting of a mixture of nonreacting substances. How many independent variables does this system have?

We can prepare the mixture with various amounts of each substance, and we are able to adjust the temperature and pressure to whatever values we wish (within certain limits that prevent the formation of a second phase). Each choice of temperature, pressure, and amounts results in a definite value of every other property, such as volume, density, and mole fraction composition. Thus, an open single-phase system of C substances has $2 + C$ independent variables. [3]

Footnote

3. C in this kind of system is actually the number of components. The number of components is usually the same as the number of substances, but is less if certain constraints exist, such as reaction equilibrium or a fixed mixture composition. The general meaning of C will be discussed in Sec. 13.

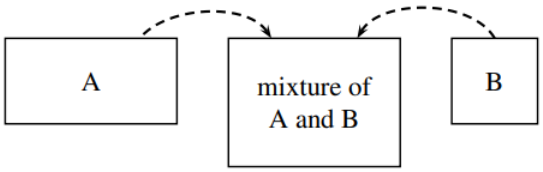


Figure 5.2.2: Mixing of water (A) and methanol (B) in a 2:1 ratio of volumes to form a mixture of increasing volume and constant composition. The system is the mixture.

For a binary mixture ($C = 2$), the number of independent variables is four. We may choose these variables to be T, p, n_A, and n_B, and write the total differential of V in the general form

$$\begin{aligned} dV = &\left(\frac{\partial V}{\partial T}\right)_{p,n_A,n_B} dT + \left(\frac{\partial V}{\partial p}\right)_{T,n_A,n_B} dp \\ &+ \left(\frac{\partial V}{\partial n_A}\right)_{T,p,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{T,p,n_A} dn_B \end{aligned} \tag{5.2.1}$$

(binary mixture)

We know the first two partial derivatives on the right side are given by [4]

Footnote

4. See Eqs. 7.1.1 and 7.1.2, which are for closed syste

$$\left(\frac{\partial V}{\partial T}\right)_{p,n_A,n_B} = \alpha V \quad \left(\frac{\partial V}{\partial p}\right)_{T,n_A,n_B} = -\kappa_T V \tag{5.2.2}$$

We identify the last two partial derivatives on the right side of Eq. 9.2.5 as the partial molar volumes V_A and V_B. Thus, we may write the total differential of V for this open system in the compact form

$$dV = \alpha V\, dT - \kappa_T V\, dp + V_A dn_A + V_B dn_B \tag{5.2.3}$$

(binary mixture)

If we compare this equation with the total differential of V for a one-component closed system, $dV = \alpha V\, dT - \kappa_T V\, dp$ (Eq. 7.1.6), we see that an additional term is required for each constituent of the mixture to allow the system to be open and the composition to vary.

When T and p are held constant, Eq. 9.2.7 becomes

$$dV = V_A dn_A + V_B dn_B \tag{5.2.4}$$

(binary mixture, constant T and p)

We obtain an important relation between the mixture volume and the partial molar volumes by imagining the following process. Suppose we continuously pour pure water and pure methanol at constant but not necessarily equal volume rates into a stirred, thermostatted container to form a mixture of increasing volume and constant composition, as shown schematically in Fig. 9.2. If this mixture remains at constant T and p as it is formed, none of its intensive properties change during the process, and the partial molar volumes V_A and V_B remain constant. Under these conditions, we can integrate Eq. 9.2.8 to obtain the additivity

rule for volume: [5]

$$V = V_A n_A + V_B n_B \tag{5.2.5}$$

(binary mixture)

This equation allows us to calculate the mixture volume from the amounts of the constituents and the appropriate partial molar volumes for the particular temperature, pressure, and composition.

For example, given that the partial molar volumes in a water-methanol mixture of composition $x_B = 0.307$ are $V_A = 17.74\ \text{cm}^3\ \text{mol}^{-1}$ and $V_B = 38.76\ \text{cm}^3\ \text{mol}^{-1}$, we calculate the volume of the water-methanol mixture described at the beginning of Sec. 9.2.1 as follows:

$$\begin{aligned} V &= \left(17.74\ \text{cm}^3\ \text{mol}^{-1}\right)(5.53\ \text{mol}) + \left(38.76\ \text{cm}^3\ \text{mol}^{-1}\right)(2.45\ \text{mol}) \\ &= 193.1\ \text{cm}^3 \end{aligned} \tag{5.2.6}$$

We can differentiate Eq. 9.2.9 to obtain a general expression for $\mathrm{d}V$ under conditions of constant T and p :

$$\mathrm{d}V = V_A \mathrm{d}n_A + V_B \mathrm{d}n_B + n_A \mathrm{d}V_A + n_B \mathrm{d}V_B \tag{5.2.7}$$

But this expression for $\mathrm{d}V$ is consistent with Eq. 9.2.8 only if the sum of the last two terms on the right is zero:

$$n_A \mathrm{d}V_A + n_B \mathrm{d}V_B = 0 \tag{5.2.8}$$

(binary mixture, constant T and p)
Equation 9.2.12 is the Gibbs-Duhem equation for a binary mixture, applied to partial molar volumes. (Section 9.2.4 will give a general version of this equation.) Dividing both sides of the equation by $n_A + n_B$ gives the equivalent form

$$x_A \mathrm{d}V_A + x_B \mathrm{d}V_B = 0 \tag{5.2.9}$$

(binary mixture, constant T and p)
Equation 9.2.12 shows that changes in the values of V_A and V_B are related when the composition changes at constant T and p. If we rearrange the equation to the form

$$\mathrm{d}V_A = -\frac{n_B}{n_A}\mathrm{d}V_B \tag{5.2.10}$$

(binary mixture, constant T and p)
we see that a composition change that increases V_B (so that $\mathrm{d}V_B$ is positive) must make V_A decrease.

Evaluation of partial molar volumes in binary mixtures

The partial molar volumes V_A and V_B in a binary mixture can be evaluated by the method of intercepts. To use this method, we plot experimental values of the quantity V/n (where n is $n_A + n_B$) versus the mole fraction x_B.V/n is called the mean molar volume.

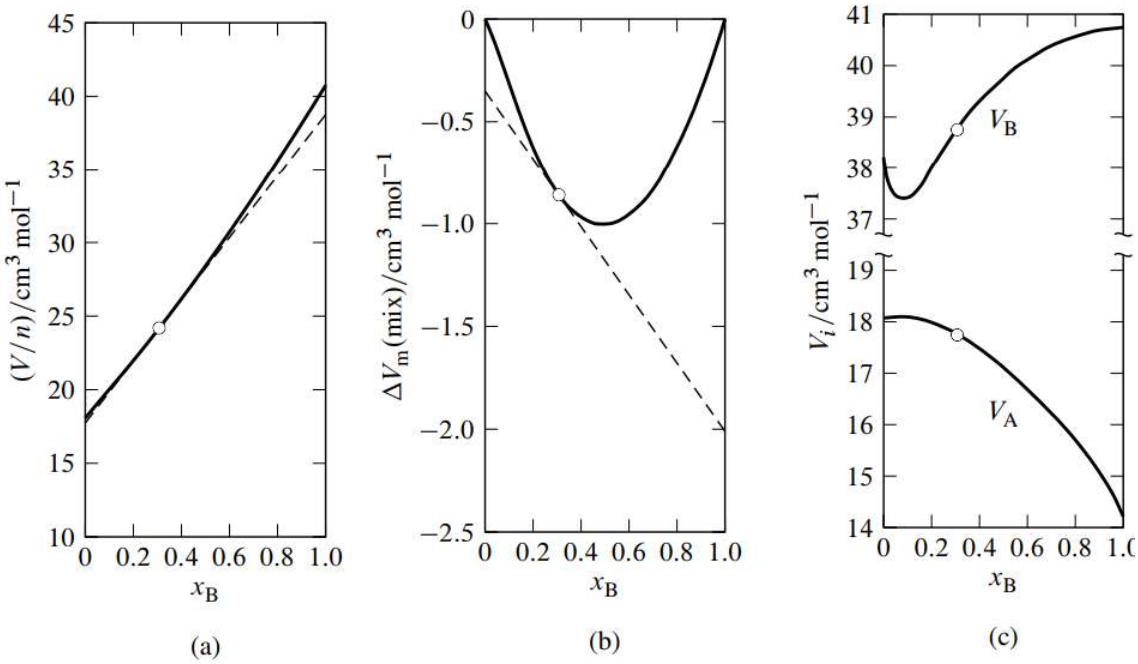


Figure **5.2.3**: Figure 9.3 Mixtures of water (A) and methanol (B) at **25°C** and 1 bar. [a]

a. Mean molar volume as a function of x_B. The dashed line is the tangent to the curve at $x_B = 0.307$.
b. Molar volume of mixing as a function of x_B. The dashed line is the tangent to the curve at $x_B = 0.307$.
c. Partial molar volumes as functions of x_B. The points at $x_B = 0.307$ (open circles) are obtained from the intercepts of the dashed line in either (a) or (b).

[a] Based on data in Ref. [12].

See Fig. 9.3(a) for an example. In this figure, the tangent to the curve drawn at the point on the curve at the composition of interest (the composition used as an illustration in Sec. 9.2.1) intercepts the vertical line where x_B equals **0** at $V/n = V_A = 17.7\,cm^3\ mol^{-1}$, and intercepts the vertical line where x_B equals **1** at $V/n = V_B = 38.8\,cm^3\ mol^{-1}$.

To derive this property of a tangent line for the plot of V/n versus x_B, we use Eq. 9.2.9 to write

$$\begin{aligned}(V/n) &= \frac{V_A n_A + V_B n_B}{n} = V_A x_A + V_B x_B \\ &= V_A(1 - x_B) + V_B x_B = (V_B - V_A)x_B + V_A\end{aligned} \tag{9.2.15}$$

Footnote

[5] The equation is an example of the result of applying Euler's theorem on homogeneous functions to V treated as a function of n_A and n_B.

When we differentiate this expression for V/n with respect to x_B, keeping in mind that V_A and V_B are functions of x_B, we obtain

$$\begin{aligned}\frac{d(V/n)}{dx_B} &= \frac{d[(V_B - V_A)x_B + V_A]}{dx_B} \\ &= V_B - V_A + \left(\frac{dV_B}{dx_B} - \frac{dV_A}{dx_B}\right)x_B + \frac{dV_A}{dx_B} \\ &= V_B - V_A + \left(\frac{dV_A}{dx_B}\right)(1 - x_B) + \left(\frac{dV_B}{dx_B}\right)x_B \\ &= V_B - V_A + \left(\frac{dV_A}{dx_B}\right)x_A + \left(\frac{dV_B}{dx_B}\right)x_B\end{aligned} \tag{9.2.16}$$

The differentials dV_A and dV_B are related to one another by the Gibbs–Duhem equation (Eq. 9.2.13): $x_A\,dV_A + x_B\,dV_B = 0$. We divide both sides of this equation by dx_B to obtain

$$\left(\frac{dV_A}{dx_B}\right)x_A + \left(\frac{dV_B}{dx_B}\right)x_B = 0 \tag{9.2.17}$$

and substitute in Eq. 9.2.16 to obtain

$$\frac{d(V/n)}{dx_B} = V_B - V_A \tag{9.2.18}$$

Let the partial molar volumes of the constituents of a binary mixture of arbitrary composition x'_B be V'_A and V'_B. Equation 9.2.15 shows that the value of V/n at the point on the curve of V/n versus x_B where the composition is x'_B is $(V'_B - V'_A)x'_B + V'_A$. Equation 9.2.18 shows that the tangent to the curve at this point has a slope of $V'_B - V'_A$. The equation of the line that passes through this point and has this slope, and thus is the tangent to the curve at this point, is $y = (V'_B - V'_A)x_B + V'_A$, where y is the vertical ordinate on the plot of (V/n) versus x_B. The line has intercepts $y{=}V'_A$ at $x_B{=}0$ and $y{=}V'_B$ at $x_B{=}1$.

A variant of the method of intercepts is to plot the molar integral volume of mixing given by

$$\Delta V_m(\text{mix}) = \frac{\Delta V(\text{mix})}{n} = \frac{V - n_A V^*_{m,A} - n_B V^*_{m,B}}{n} \tag{9.2.19}$$

versus x_B, as illustrated in Fig. 9.3(b). $\Delta V(\text{mix})$ is the integral volume of mixing—the volume change at constant T and p when solvent and solute are mixed to form a mixture of volume V and total amount n (see Sec. 11.1.1). The tangent to the curve at the composition of interest has intercepts $V_A - V^*_{m,A}$ at $x_B{=}0$ and $V_B - V^*_{m,B}$ at $x_B{=}1$.

To see this, we write

$$\begin{aligned}\Delta V_m(\text{mix}) &= (V/n) - x_A V^*_{m,A} - x_B V^*_{m,B} \\ &= (V/n) - (1 - x_B)V^*_{m,A} - x_B V^*_{m,B}\end{aligned} \tag{9.2.20}$$

We make the substitution $(V/n) = (V_B - V_A)x_B + V_A$ from Eq. 9.2.15 and rearrange:

$$\Delta V_m(\text{mix}) = \left[(V_B - V^*_{m,B}) - (V_A - V^*_{m,A})\right]x_B + (V_A - V^*_{m,A}) \tag{9.2.21}$$

Differentiation with respect to x_B yields

$$\begin{aligned}\frac{d\Delta V_m(\text{mix})}{dx_B} &= (V_B - V^*_{m,B}) - (V_A - V^*_{m,A}) + \left(\frac{dV_B}{dx_B} - \frac{dV_A}{dx_B}\right)x_B + \frac{dV_A}{dx_B} \\ &= (V_B - V^*_{m,B}) - (V_A - V^*_{m,A}) + \left(\frac{dV_A}{dx_B}\right)(1 - x_B) + \left(\frac{dV_B}{dx_B}\right)x_B \\ &= (V_B - V^*_{m,B}) - (V_A - V^*_{m,A}) + \left(\frac{dV_A}{dx_B}\right)x_A + \left(\frac{dV_B}{dx_B}\right)x_B\end{aligned} \tag{9.2.22}$$

With a substitution from Eq. 9.2.17, this becomes

$$\frac{d\Delta V_m(\text{mix})}{dx_B} = (V_B - V^*_{m,B}) - (V_A - V^*_{m,A}) \tag{9.2.23}$$

Equations 9.2.21 and 9.2.23 are analogous to Eqs. 9.2.15 and 9.2.18, with V/n replaced by $\Delta V_m(\text{mix})$, V_A by $(V_A - V^*_{m,A})$, and V_B by $(V_B - V^*_{m,B})$. Using the same reasoning as for a plot of V/n versus x_B, we find the intercepts of the tangent to a point on the curve of $\Delta V_m(\text{mix})$ versus x_B are at $V_A - V^*_{m,A}$ and $V_B - V^*_{m,B}$.

Figure 9.3 shows smoothed experimental data for water–methanol mixtures plotted in both kinds of graphs, and the resulting partial molar volumes as functions of composition. Note in Fig. 9.3(c) how the V_A curve mirrors the V_B curve as x_B varies, as predicted by the Gibbs–Duhem equation. The minimum in V_B at $x_B \approx 0.09$ is mirrored by a maximum in V_A in agreement with Eq. 9.2.14; the maximum is much attenuated because n_B/n_A is much less than unity.

Macroscopic measurements are unable to provide unambiguous information about molecular structure. Nevertheless, it is interesting to speculate on the implications of the minimum observed for the partial molar volume of methanol.

One interpretation is that in a mostly aqueous environment, there is association of methanol molecules, perhaps involving the formation of dimers.

General relations

The discussion above of partial molar volumes used the notation $V^*_{m,A}$ and $V^*_{m,B}$ for the molar volumes of pure A and B. The partial molar volume of a pure substance is the same as the molar volume, so we can simplify the notation by using V^*_A and V^*_B instead. Hereafter, this e-book will denote molar quantities of pure substances by such symbols as V^*_A, H^*_B, and S^*_i.

The relations derived above for the volume of a binary mixture may be generalized for any extensive property X of a mixture of any number of constituents. The partial molar quantity of species i, defined by

$$X_i \overset{\text{def}}{=} \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{9.2.24}$$

is an intensive property that depends on T, p, and the composition of the mixture. The additivity rule for property X is

$$X = \sum_i n_i X_i \qquad \begin{matrix}(9.2.25)\\(\text{mixture})\end{matrix}$$

and the Gibbs–Duhem equation applied to X can be written in the equivalent forms

$$\sum_i n_i \, \mathrm{d}X_i = 0 \qquad \begin{matrix}(9.2.26)\\(\text{constant } T \text{ and } p)\end{matrix}$$

and

$$\sum_i x_i \, \mathrm{d}X_i = 0 \qquad \begin{matrix}(9.2.27)\\(\text{constant } T \text{ and } p)\end{matrix}$$

These relations can be applied to a mixture in which each species i is a nonelectrolyte substance, an electrolyte substance that is dissociated into ions, or an individual ionic species. In Eq. 9.2.27, the mole fraction x_i must be based on the different species considered to be present in the mixture. For example, an aqueous solution of NaCl could be treated as a mixture of components A=H_2O and B=NaCl, with x_B equal to $n_B/(n_A + n_B)$; or the constituents could be taken as H_2O, Na^+, and Cl^-, in which case the mole fraction of Na^+ would be $x_+ = n_+/(n_A + n_+ + n_-)$.

A general method to evaluate the partial molar quantities X_A and X_B in a binary mixture is based on the variant of the method of intercepts described in Sec. 9.2.3. The molar mixing quantity $\Delta X(\text{mix})/n$ is plotted versus x_B, where $\Delta X(\text{mix})$ is $(X - n_A X^*_A - n_B X^*_B)$. On this plot, the tangent to the curve at the composition of interest has intercepts equal to $X_A - X^*_A$ at $x_B = 0$ and $X_B - X^*_B$ at $x_B = 1$.

We can obtain experimental values of such partial molar quantities of an uncharged species as V_i, $C_{p,i}$, and S_i. It is not possible, however, to evaluate the partial molar quantities U_i, H_i, A_i, and G_i because these quantities involve the internal energy brought into the system by the species, and we cannot evaluate the absolute value of internal energy (Sec. 2.6.2). For example, while we can evaluate the difference $H_i - H^*_i$ from calorimetric measurements of enthalpies of mixing, we cannot evaluate the partial molar enthalpy H_i itself. We can, however, include such quantities as H_i in useful theoretical relations.

A partial molar quantity of a *charged* species is something else we cannot evaluate. It is possible, however, to obtain values relative to a reference ion. Consider an aqueous solution of a fully-dissociated electrolyte solute with the formula $\mathrm{M}_{\nu_+}\mathrm{X}_{\nu_-}$, where ν_+ and ν_- are the numbers of cations and anions per solute formula unit. The partial molar volume V_B of the solute, which can be determined experimentally, is related to the (unmeasurable) partial molar volumes V_+ and V_- of the constituent ions by

$$V_B = \nu_+ V_+ + \nu_- V_- \tag{9.2.28}$$

For aqueous solutions, the usual reference ion is H^+, and the partial molar volume of this ion at infinite dilution is arbitrarily set equal to zero: $V^\infty_{H^+} = 0$.

For example, given the value (at 298.15 K and 1 bar) of the partial molar volume at infinite dilution of aqueous hydrogen chloride

$$V^{\infty}_{\mathrm{HCl}} = 17.82\,\mathrm{cm^3\ mol^{-1}} \tag{9.2.29}$$

we can find the so-called "conventional" partial molar volume of Cl^- ion:

$$V^{\infty}_{\mathrm{Cl^-}} = V^{\infty}_{\mathrm{HCl}} - V^{\infty}_{\mathrm{H^+}} = 17.82\,\mathrm{cm^3\ mol^{-1}} \tag{9.2.30}$$

Going one step further, the measured value $V^{\infty}_{\mathrm{NaCl}} = 16.61\,\mathrm{cm^3\ mol^{-1}}$ gives, for Na^+ ion, the conventional value

$$V^{\infty}_{\mathrm{Na^+}} = V^{\infty}_{\mathrm{NaCl}} - V^{\infty}_{\mathrm{Cl^-}} = (16.61 - 17.82)\,\mathrm{cm^3\ mol^{-1}} = -1.21\,\mathrm{cm^3\ mol^{-1}} \tag{9.2.31}$$

Partial specific quantities

A **partial specific quantity** of a substance is the partial molar quantity divided by the molar mass, and has dimensions of volume divided by mass. For example, the partial specific volume v_{B} of solute B in a binary solution is given by

$$v_{\mathrm{B}} = \frac{V_{\mathrm{B}}}{M_{\mathrm{B}}} = \left[\frac{\partial V}{\partial m(\mathrm{B})}\right]_{T,p,m(\mathrm{A})} \tag{9.2.32}$$

where $m(\mathrm{A})$ and $m(\mathrm{B})$ are the masses of solvent and solute.

Although this e-book makes little use of specific quantities and partial specific quantities, in some applications they have an advantage over molar quantities and partial molar quantities because they can be evaluated without knowledge of the molar mass. For instance, the value of a solute's partial specific volume is used to determine its molar mass by the method of sedimentation equilibrium (Sec. 9.8.2).

The general relations in Sec. 9.2.4 involving partial molar quantities may be turned into relations involving partial specific quantities by replacing amounts by masses, mole fractions by mass fractions, and partial molar quantities by partial specific quantities. Using volume as an example, we can write an additivity relation $V = \sum_i m(i)v_i$, and Gibbs–Duhem relations $\sum_i m(i)\,\mathrm{d}v_i = 0$ and $\sum_i w_i\,\mathrm{d}v_i = 0$. For a binary mixture of A and B, we can plot the specific volume v versus the mass fraction w_{B}; then the tangent to the curve at a given composition has intercepts equal to v_{A} at $w_{\mathrm{B}} = 0$ and v_{B} at $w_{\mathrm{B}} = 1$. A variant of this plot is $(v - w_{\mathrm{A}}v^*_{\mathrm{A}} - w_{\mathrm{B}}v^*_{\mathrm{B}})$ versus w_{B}; the intercepts are then equal to $v_{\mathrm{A}} - v^*_{\mathrm{A}}$ and $v_{\mathrm{B}} - v^*_{\mathrm{B}}$.

Chemical potential is an important partial molar quantity

Just as the molar Gibbs energy of a pure substance is called the *chemical potential* and given the special symbol μ, the partial molar Gibbs energy G_i of species i in a mixture is called the **chemical potential** of species i, defined by

$$\mu_i \stackrel{\text{def}}{=} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{9.2.33}$$
$$(\text{mixture})$$

If there are work coordinates for nonexpansion work, the partial derivative is taken at constant values of these coordinates.

The chemical potential of a species in a phase plays a crucial role in equilibrium problems, because it is a measure of the escaping tendency of the species from the phase. Although we cannot determine the absolute value of μ_i for a given state of the system, we are usually able to evaluate the difference between the value in this state and the value in a defined reference state.

In an open single-phase system containing a mixture of s different nonreacting species, we may in principle independently vary T, p, and the amount of each species. This is a total of $2 + s$ independent variables. The total differential of the Gibbs energy of this system is given by Eq. 5.5.9, often called the Gibbs fundamental equation:

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_{i=1}^{s}\mu_i\,\mathrm{d}n_i \tag{9.2.34}$$
$$(\text{mixture})$$

Consider the special case of a mixture containing *charged* species, for example an aqueous solution of the electrolyte KCl. We could consider the constituents to be either the substances H_2O and KCl, or else H_2O and the species K^+ and Cl^-. Any mixture we can prepare in the laboratory must remain electrically neutral, or virtually so. Thus, while we are able to independently vary the amounts of H_2O and KCl, we cannot in practice independently vary the amounts of K^+ and Cl^- in the mixture. The chemical potential of the K^+ ion is defined as the rate at which the Gibbs energy changes with the amount of K^+ added at constant T and p while the amount of Cl^- is kept constant. This is a hypothetical process in which the net charge of the mixture increases. The

chemical potential of a ion is therefore a valid but purely theoretical concept. Let A stand for H_2O, B for KCl, + for K^+, and − for Cl^-. Then it is theoretically valid to write the total differential of G for the KCl solution either as

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} \tag{9.2.35}$$

or as

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_+\,\mathrm{d}n_+ + \mu_-\,\mathrm{d}n_- \tag{9.2.36}$$

Relations involving partial molar quantities

Here we derive several useful relations involving partial molar quantities in a single-phase system that is a mixture. The independent variables are T, p, and the amount n_i of each constituent species i.

From Eqs. 9.2.26 and 9.2.27, the Gibbs–Duhem equation applied to the chemical potentials can be written in the equivalent forms

$$\sum_i n_i\,\mathrm{d}\mu_i = 0 \qquad \text{(constant } T \text{ and } p\text{)} \tag{9.2.42}$$

and

$$\sum_i x_i\,\mathrm{d}\mu_i = 0 \qquad \text{(constant } T \text{ and } p\text{)} \tag{9.2.43}$$

These equations show that the chemical potentials of different species cannot be varied independently at constant T and p.

A more general version of the Gibbs–Duhem equation, without the restriction of constant T and p, is

$$S\,\mathrm{d}T - V\,\mathrm{d}p + \sum_i n_i\,\mathrm{d}\mu_i = 0 \tag{9.2.44}$$

This version is derived by comparing the expression for $\mathrm{d}G$ given by Eq. 9.2.34 with the differential $\mathrm{d}G = \sum_i \mu_i\,\mathrm{d}n_i + \sum_i n_i\,\mathrm{d}\mu_i$ obtained from the additivity rule $G = \sum_i \mu_i n_i$.

The Gibbs energy is defined by $G = H - TS$. Taking the partial derivatives of both sides of this equation with respect to n_i at constant T, p, and $n_{j\neq i}$ gives us

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{9.2.45}$$

We recognize each partial derivative as a partial molar quantity and rewrite the equation as

$$\mu_i = H_i - TS_i \tag{9.2.46}$$

This is analogous to the relation $\mu = G/n = H_\mathrm{m} - TS_\mathrm{m}$ for a pure substance.

From the total differential of the Gibbs energy, $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i$ (Eq. 9.2.34), we obtain the following reciprocity relations:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\{n_i\}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{n_i\}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{9.2.47}$$

The symbol $\{n_i\}$ stands for the set of amounts of all species, and subscript $\{n_i\}$ on a partial derivative means the amount of *each* species is constant—that is, the derivative is taken at constant composition of a closed system. Again we recognize partial derivatives as partial molar quantities and rewrite these relations as follows:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\{n_i\}} = -S_i \tag{9.2.48}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{n_i\}} = V_i \tag{9.2.49}$$

These equations are the equivalent for a mixture of the relations $(\partial\mu/\partial T)_p = -S_\mathrm{m}$ and $(\partial\mu/\partial p)_T = V_\mathrm{m}$ for a pure phase (Eqs. 7.8.3 and 7.8.4).

Taking the partial derivatives of both sides of $U = H - pV$ with respect to n_i at constant T, p, and $n_{j \neq i}$ gives

$$U_i = H_i - pV_i \tag{9.2.50}$$

Finally, we can obtain a formula for $C_{p,i}$, the partial molar heat capacity at constant pressure of species i, by writing the total differential of H in the form

$$\begin{aligned} \mathrm{d}H &= \left(\frac{\partial H}{\partial T}\right)_{p,\{n_i\}} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\{n_i\}} \mathrm{d}p + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_{j \neq i}} \mathrm{d}n_i \\ &= C_p \, \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\{n_i\}} \mathrm{d}p + \sum_i H_i \, \mathrm{d}n_i \end{aligned} \tag{9.2.51}$$

from which we have the reciprocity relation $(\partial C_p / \partial n_i)_{T,p,n_{j \neq i}} = (\partial H_i / \partial T)_{p,\{n_i\}}$, or

$$C_{p,i} = \left(\frac{\partial H_i}{\partial T}\right)_{p,\{n_i\}} \tag{9.2.52}$$

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5.3: Ideal Solutions obey Raoult's Law

Liquids tend to be volatile, and as such will enter the vapor phase when the temperature is increased to a high enough value, provided they do not decompose first. A volatile liquid is one that has an appreciable vapor pressure at the specified temperature. An ideal mixture containing at least one volatile liquid can be described using **Raoult's Law:**

$$P_j = x_j P_j^*$$

Raoult's law can be used to predict the total vapor pressure above a mixture of two volatile liquids. As it turns out, the composition of the vapor will be different than that of the two liquids, with the more volatile compound having a larger mole fraction in the vapor phase than in the liquid phase. This is summarized in the following diagram for an ideal mixture of two compounds, water and ethanol at 75 °C. At this temperature, water a pure vapor pressure of 384 Torr and ethanol has a pure vapor pressure of 945 Torr. In Figure 24.4.1, the composition of the liquid phase is represented by the solid line and the composition of the vapor phase is represented by the dashed line.

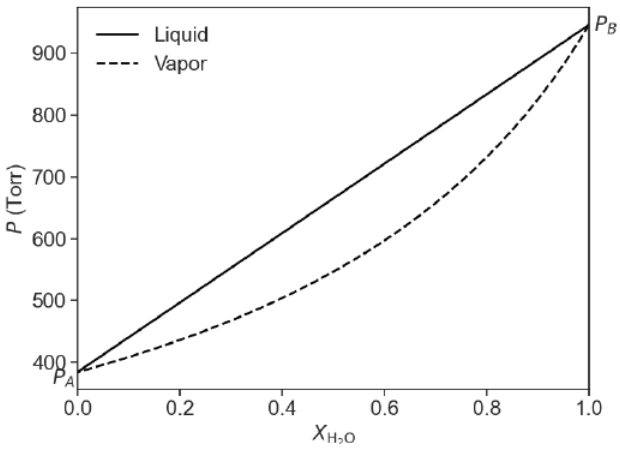


Figure 24.4.1: The composition of the liquid phase (solid line) and the vapor phase (dashed lined) as a function of mole fraction according to Raoult's law. The solution is a mixture of water and ethanol. P_A is the vapor pressure of pure water and P_B is the vapor pressure of pure ethanol at 75 °C

Often, it is desirable to depict the phase diagram at a single pressure so that temperature and composition are the variables included in the graphical representation. In such a diagram, the vapor, which exists at higher temperatures) is indicated at the top of the diagram, while the liquid is at the bottom. A typical temperature vs. composition diagram is depicted in Figure 24.4.2 for an ideal mixture of two volatile liquids.

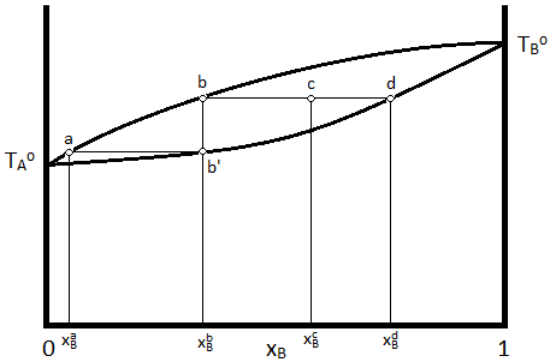


Figure 24.4.2: A typical temperature vs. composition diagram.

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In this diagram, T_A and T_B represent the boiling points of pure compounds A and B. If a system having the composition indicated by χ_B^c has its temperature increased to that indicated by point c, The system will consist of two phases, a liquid phase, with a composition indicated by χ_B^d and a vapor phase indicated with a composition indicated by χ_B^b. The relative amounts of material in each phase can be described by the lever rule, as described previously.

Further, if the vapor with composition χ_B^b is condensed (the temperature is lowered to that indicated by point b') and re-vaporized, the new vapor will have the composition consistent with χ_B^a. This demonstrates how the more volatile liquid (the one with the lower boiling temperature, which is A in the case of the above diagram) can be purified from the mixture by collecting and re-evaporating fractions of the vapor. If the liquid was the desired product, one would collect fractions of the residual liquid to achieve the desired result. This process is known as distillation.

The Gibbs energy of mixing is always negative

When we add n_A moles of component A and n_B moles of component B to form an ideal liquid solution, this is generally a spontaneous process. Let us consider the Gibbs free energy change of that process:

$$\Delta_{mix}G = n_1\mu_1^{sln} + n_2\mu_2^{sln} - (n_1\mu_1^* + n_2\mu_2^*)$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + nRTx_i \ln x_i$$

his expression simplifies to:

$$\Delta_{mix}G = nRTx_A \ln x_A + nRTx_B \ln x_B$$

where n is the total moles. Mole fraction, x_i, is always less than one, so the Gibbs energy of mixing is always negative; mixing is always spontaneous. We can generalize this to mixtures with more than two components:

$$\Delta_{mix}G = nRT\sum_i x_i \ln x_i$$

This expression looks suspiciously familiar. Apart from a factor of $-T$, it is just like the **entropy of mixing**:

$$\Delta_{mix}S = -nR\sum_i x_i \ln x_i$$

Recalling the relationship between Gibbs energy and entropy:

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$$

This leaves no room at all for an enthalpy effect:

$$\Delta_{mix}H = 0$$

Even though there are strong interactions between neighboring particles in liquids, there is no enthalpy change. This implies that it does not matter what the neighboring molecules are. If we represent the average interaction energy between molecule i and j by U_{ij}, we are assuming that U_{ij} is always the same. In practice, this is *seldom* the case. It usually does matter and then the enthalpy term is not zero. As this affects the thermodynamics of the liquid solution, it should also affect the vapor pressures that are in equilibrium with it.

In the ideal case, volumes are additive

From the change of G in its natural variables, we know that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

This means that if we take

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V_{mix}$$

In the ideal case we get:

$$\left(\frac{\partial \Delta G^{ideal}}{\partial P}\right)_T = \Delta V_{mix}^{ideal}$$

$$\left(\frac{\partial RT(n_1 \ln x_1 + n_2 \ln x_2)}{\partial P}\right)_T = \Delta V_{mix}^{ideal} = 0$$

In the ideal case, volumes are *additive* and we need not worry about how the partial molar volumes change with composition.

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5.4: Most Solutions are Not Ideal

If we plot the partial pressure of one component, P_1, above a mixture with a mole fraction x_1, we should get a straight line with a slope of P_1^* (Raoult's law). Above non-ideal solutions the graph will no longer be a straight line but a curve. However towards $x_1 = 1$ the curve typically approaches the Raoult line. On the other extreme, there often is a more or less linear region as well, ***but with a different slope*** (Figure 24.5.1). This means that we can identify two *limiting* laws:

- For $x \to 0$: **Henry's law**:

$$P_1 = K_H x_1$$

- For $x \to 1$: **Raoult's law**:

$$P_1 = P_1^* x_1$$

This implies that the straight line that indicates the Henry expression will intersect the y-axis at $x = 1$ (pure compound) at a ***different*** point than P^*. For $x \to 0$ (low concentrations) we can speak of component 1 being the *solute* (the minority component). At the other end $x \to 1$ it plays the role of the *solvent* (majority component).

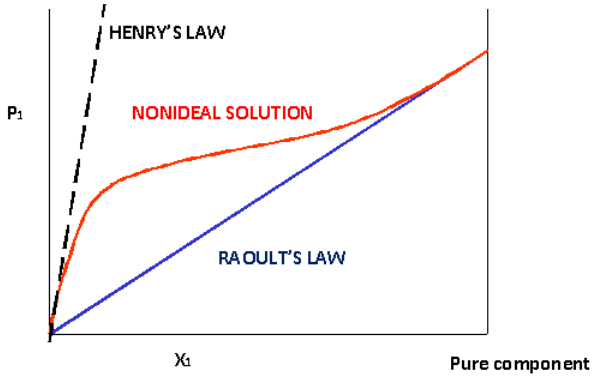


Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> Another thing to note is that P^* is a property of *one pure component*, the value of K_H by contrast is a property of the *combination of two components*, so it needs to be measured for each solute-solvent combination.

As you can see we have a description for both the high and the low end, but not in the middle. In general, the more modest the deviations from ideality the larger the range of validity of the two limiting laws. The way to determine K_H would be to actually determine vapor pressures. How about the other component? Do we need to measure them too? Fortunately we can use thermodynamics to answer this question with no. There is a handy expression that saves us the trouble.

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5.5: The Activities of Nonvolatile Solutes

For non-ideal gases, we introduced in chapter 11 the concept of *fugacity* as an *effective pressure* that accounts for non-ideal behavior. If we extend this concept to non-ideal solution, we can introduce the *activity* of a liquid or a solid, a, as:

$$\mu_{\text{non-ideal}} = \mu^{-\ominus} + RT \ln a, \tag{5.5.1}$$

where μ is the chemical potential of the substance or the mixture, and $\mu^{-\ominus}$ is the chemical potential at standard state. Comparing this definition to Equation 11.4.2, it is clear that the activity is equal to the fugacity for a non-ideal gas (which, in turn, is equal to the pressure for an ideal gas). However, for a liquid and a liquid mixture, it depends on the chemical potential at standard state. This means that the activity is not an absolute quantity, but rather a relative term describing how "active" a compound is compared to standard state conditions. The choice of the standard state is, in principle, arbitrary, but conventions are often chosen out of mathematical or experimental convenience. We already discussed the convention that standard state for a gas is at $P^{-\ominus} = 1$ bar, so the activity is equal to the fugacity. The standard state for a component in a solution is the pure component at the temperature and pressure of the solution. This definition is equivalent to setting the activity of a pure component, i, at $a_i = 1$.

For a component in a solution we can use Equation 11.4.2 to write the chemical potential in the gas phase as:

$$\mu_i^{\text{vapor}} = \mu_i^{-\ominus} + RT \ln \frac{P_i}{P^{-\ominus}}. \tag{5.5.2}$$

If the gas phase is in equilibrium with the liquid solution, then:

$$\mu_i^{\text{solution}} = \mu_i^{\text{vapor}} = \mu_i^*, \tag{5.5.3}$$

where μ_i^* is the chemical potential of the pure element. Subtracting Equation 5.5.3 from Equation 5.5.2, we obtain:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}. \tag{5.5.4}$$

For an ideal solution, we can use Raoult's law, Equation 13.1.1, to rewrite Equation 5.5.4 as:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i, \tag{5.5.5}$$

which relates the chemical potential of a component in an ideal solution to the chemical potential of the pure liquid and its mole fraction in the solution. For a non-ideal solution, the partial pressure in Equation 5.5.4 is either larger (positive deviation) or smaller (negative deviation) than the pressure calculated using Raoult's law. The chemical potential of a component in the mixture is then calculated using:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln (\gamma_i x_i), \tag{5.5.6}$$

where γ_i is a positive coefficient that accounts for deviations from ideality. This coefficient is either larger than one (for positive deviations), or smaller than one (for negative deviations). The activity of component i can be calculated as an *effective mole fraction*, using:

$$a_i = \gamma_i x_i, \tag{5.5.7}$$

where γ_i is defined as the **activity coefficient**. The partial pressure of the component can then be related to its vapor pressure, using:

$$P_i = a_i P_i^*. \tag{5.5.8}$$

Comparing Equation 5.5.8 with Raoult's law, we can calculate the activity coefficient as:

$$\gamma_i = \frac{P_i}{x_i P_i^*} = \frac{P_i}{P_i^{\text{R}}}, \tag{5.5.9}$$

where P_i^{R} is the partial pressure calculated using Raoult's law. This result also proves that for an ideal solution, $\gamma = 1$. Equation 5.5.9 can also be used experimentally to obtain the activity coefficient from the phase diagram of the non-ideal solution. This is achieved by measuring the value of the partial pressure of the vapor of a non-ideal solution. Examples of this procedure are reported for both positive and negative deviations in Figure 5.5.1.

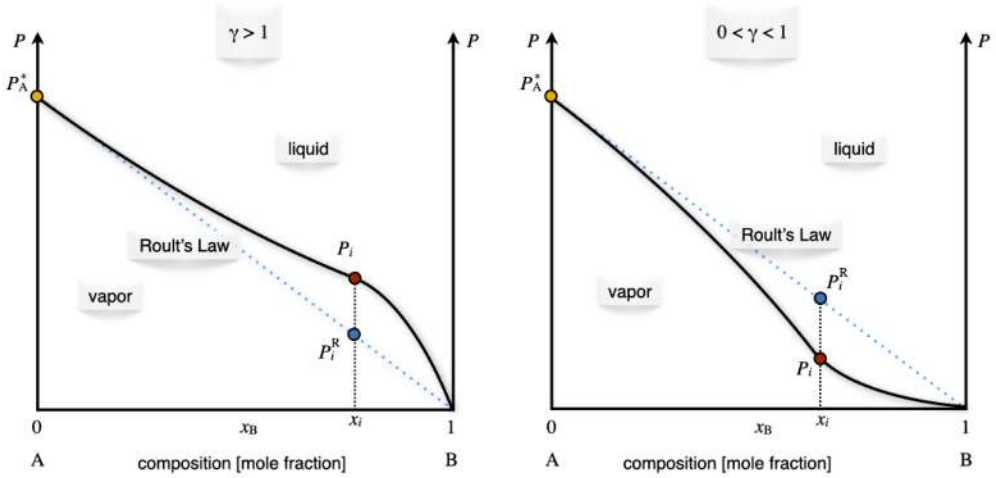


Figure 5.5.1: Positive and Negative Deviation from Raoult's Law in the Pressure–Composition Phase Diagram of Non-Ideal Solutions at Constant Temperature.

- As we already discussed in chapter 10, the activity is the most general quantity that we can use to define the equilibrium constant of a reaction (or the reaction quotient). The advantage of using the activity is that it's defined for ideal and non-ideal gases and mixtures of gases, as well as for ideal and non-ideal solutions in both the liquid and the solid phase.[1]

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1. Notice that, since the activity is a relative measure, the equilibrium constant expressed in terms of the activities is also a relative concept. In other words, it measures equilibrium relative to a standard state. This fact, however, should not surprise us, since the equilibrium constant is also related to $\Delta_{rxn}G^{-\ominus}$ using Gibbs' relation. This is why the definition of a universally agreed-upon standard state is such an essential concept in chemistry, and why it is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe.

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5.6: Colligative Properties Depend only on Number Density

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

- **Solution** – a homogeneous mixture.
- **Solvent** – The component of a solution with the largest mole fraction
- **Solute** – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous forms. For the most part, this discussion will focus on liquid-phase solutions.

Freezing Point Depression

In general (and as will be discussed in Chapter 8 in more detail) a liquid will freeze when

$$\mu_{solid} \leq \mu_{liquid}$$

As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent. As it turns out, the chemical potential of the solvent is reduced by the presence of a solute.

In a mixture, the chemical potential of component A can be calculated by

$$\mu_A = \mu_A^o + RT \ln \chi_A \tag{5.6.1}$$

And because χ_A is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

The condition under which the solvent will freeze is

$$\mu_{A,solid} = \mu_{A,liquid}$$

where the chemical potential of the liquid is given by Equation 5.6.1, which rearrangement to

$$\frac{\mu_A - \mu_A^o}{RT} = \ln \chi_A$$

To evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_A - \mu_A^o}{RT}\right)\right]_p = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT}\left[\left(\frac{\partial \mu_A}{\partial T}\right)_p - \left(\frac{\partial \mu_A^o}{\partial T}\right)_p\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{5.6.2}$$

Recalling that

$$\mu = H = TS$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

Equation 5.6.2 becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT}\left[-S_A + S_A^o\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{5.6.3}$$

And noting that in the case of the solvent freezing, H_A^o is the enthalpy of the pure solvent in solid form, and H_A is the enthalpy of the solvent in the liquid solution. So

$$H_A^o - H_a = \Delta H_{fus}$$

Equation 5.6.3 then becomes

$$\frac{\Delta H_{fus}}{RT^2} - \frac{\cancel{-S_A + S_A^o}}{\cancel{RT}} + \frac{\cancel{-S_A + S_A^o}}{\cancel{RT}} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

or

$$\frac{\Delta H_{fus}}{RT^2} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^{T} \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln \chi_A \tag{5.6.4}$$

where T^o is the freezing point of the pure solvent and T is the temperature at which the solvent will begin to solidify in the solution. After integration of Equation 5.6.4:

$$-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right) = \ln \chi_A \tag{5.6.5}$$

This can be simplified further by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o}$$

where ΔT is the difference between the freezing temperature of the pure solvent and that of the solvent in the solution. Also, for small deviations from the pure freezing point, TT^o can be replaced by the approximate value $(T^o)^2$. So the Equation 5.6.5 becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2}\Delta T = \ln \chi_A \tag{5.6.6}$$

Further, for dilute solutions, for which χ_A, the mole fraction of the solvent is very nearly 1, then

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

where χ_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{R(T^o)^2}{\Delta H_{fus}}\right)\chi_B$$

The first factor can be replaced by K_f:

$$\frac{R(T^o)^2}{\Delta H_{fus}} = K_f$$

which is the **cryoscopic constant** for the solvent.

ΔT gives the magnitude of the reduction of freezing point for the solution. Since ΔH_{fus} and T^o are properties of the solvent, the freezing point depression property is independent of the solute and is a property based solely on the nature of the solvent. Further, since χ_B was introduced as $(1 - \chi_A)$, it represents the sum of the mole fractions of all solutes present in the solution.

It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of ΔT will change as the freezing process continually removes solvent from the liquid phase of the solution.

Boiling Point Elevation

The derivation of an expression describing boiling point elevation is similar to that for freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, cause it to favor the liquid phase over the vapor phase. As sch, the temperature must be increased to increase the chemical potential of the solvent in the liquid solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b \chi_B$$

where

$$\frac{R(T^\circ)^2}{\Delta H_{vap}} = K_b$$

is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes. A very elegant derivation of the form of the models for freezing point depression and boiling point elevation has been shared by F. E. Schubert (Schubert, 1983).

Cryoscopic and ebullioscopic constants are generally tabulated using molality as the unit of solute concentration rather than mole fraction. In this form, the equation for calculating the magnitude of the freezing point decrease or the boiling point increase is

$$\Delta T = K_f m$$

or

$$\Delta T = K_b m$$

where m is the concentration of the solute in moles per kg of solvent. Some values of K_f and K_b are shown in the table below.

Substance	K_f (°C kg mol-1)	T_f^o (°C)	K_b (°C kg mol-1)	T_b^o (°C)
Water	1.86	0.0	0.51	100.0
Benzene	5.12	5.5	2.53	80.1
Ethanol	1.99	-114.6	1.22	78.4
CCl_4	29.8	-22.3	5.02	76.8

Example 5.6.1:

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of CCl_4 raises the boiling point to 81.5 °C. What is the molar mass of the compound?

Solution

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(85.5\,°C - 76.8\,°C) = (5.02\,°C\,Kg/mol)\,m$$

$$m = 0.936\,mol/kg$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\,mol/\cancel{kg}\right)(0.02\,\cancel{kg}) = 0.0234\,mol$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\,g}{0.0234} = 128 g/mol$$

Vapor Pressure Lowering

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{vapor} = \mu_{solvent}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu^o_{vap} + RT \ln \frac{p'}{p^o} = \mu^o_A + RT \ln \chi_A \tag{5.6.7}$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu^o_A = \mu^o_{vap} + RT \ln \frac{p_A}{p^o} \tag{5.6.8}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substituting Equation 5.6.8 into Equation 5.6.7 yields

$$\cancel{\mu^o_{vap}} + RT \ln \frac{p'}{p^o} = \left(\cancel{\mu^o_{vap}} + RT \ln \frac{p_A}{p^o} \right) + RT \ln \chi_A$$

The terms for μ^o_{vap} cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln \chi_A$$

Subtracting $RT \ln(P_A/P^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln \chi_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln \chi_A$$

Dividing both sides by RT and then exponentiating yields

$$\frac{p'}{p_A} = \chi_A$$

or

$$p' = \chi_A p_A \tag{5.6.9}$$

This last result is Raoult's Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

Example 5.6.2:

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

Solution

Using Raoult's Law (Equation 5.6.9)

$$p_A = (0.400)(150\,Toor) = 60.0\,Torr$$

$$p_B = (0.600)(300\,Toor) = 180.0\,Torr$$

$$p_{tot} = p_A + p_B = 240\,Torr$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

$$\chi_A = \frac{p_A}{p_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

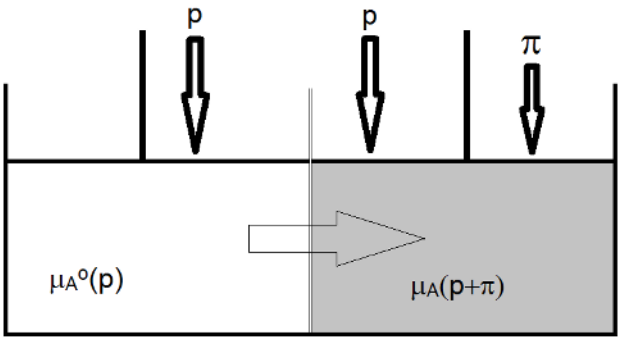
$$\chi_B = \frac{p_B}{p_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$\chi_A + \chi_B = 1$$

Osmotic Pressure

Osmosis is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln \chi_A$$

And since $x_A < 1$, the chemical potential is of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(\chi_b, +\pi)$$

To solve the problem to determine the magnitude of p, the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure p must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = RT \ln \chi_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p+\pi) = \mu(p) + \int_p^\pi \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

where V is the molar volume of the substance. Combining these expressions results in

$$-RT\ln\chi_A = \int_p^{p+\pi} V\,dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of κ_T – which is the case for most liquids) the term on the right becomes.

$$\int_p^{\pi} V\,dP = Vp\Big|_p^{p+\pi} = V\pi$$

Also, for values of χ_A very close to 1

$$\ln\chi_A \approx -(1-\chi_A) = -\chi_B$$

So, for dilute solutions

$$\chi_B RT = V\pi$$

Or after rearrangement

$$\pi\frac{\chi_B RT}{V}$$

again, where V is the molar volume of the solvent. And finally, since χ_B/V is the concentration of the solute B for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure π is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

Colligative properties are properties that depend on the *number* of particles rather than their total mass. This implies that these properties can be used to measure molar mass. Colligative properties include:

- melting point depression
- boiling point elevation
- osmotic pressure

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5.7: Single-ion Quantities

Consider a solution of an electrolyte solute that dissociates completely into a cation species and an anion species. Subscripts + and − will be used to denote the cation and anion, respectively. The solute molality m_B is defined as the amount of solute formula unit divided by the mass of solvent.

We first need to investigate the relation between the chemical potential of an ion species and the electric potential of the solution phase.

The electric potential ϕ in the interior of a phase is called the *inner electric potential*, or *Galvani potential*. It is defined as the work needed to reversibly move an infinitesimal test charge into the phase from a position infinitely far from other charges, divided by the value of the test charge. The electrical potential energy of a charge in the phase is the product of ϕ and the charge.

Consider a hypothetical process in which an infinitesimal amount $\mathrm{d}n_+$ of the cation is transferred into a solution phase at constant T and p. The quantity of charge transferred is $\delta Q = z_+ F\,\mathrm{d}n_+$, where z_+ is the charge number (+1, +2, etc.) of the cation, and F is the Faraday constant. (The Faraday constant is the charge per amount of protons.) If the phase is at zero electric potential, the process causes no change in its electrical potential energy. However, if the phase has a finite electric potential ϕ, the transfer process changes its electrical potential energy by $\phi\delta Q = z_+ F\phi\,\mathrm{d}n_+$. Consequently, the internal energy change depends on ϕ according to

$$\mathrm{d}U(\phi) = \mathrm{d}U(0) + z_+ F\phi\,\mathrm{d}n_+ \tag{10.1.1}$$

where the electric potential is indicated in parentheses. The change in the Gibbs energy of the phase is given by $\mathrm{d}G = \mathrm{d}(U - TS + pV)$, where T, S, p, and V are unaffected by the value of ϕ. The dependence of $\mathrm{d}G$ on ϕ is therefore

$$\mathrm{d}G(\phi) = \mathrm{d}G(0) + z_+ F\phi\,\mathrm{d}n_+ \tag{10.1.2}$$

The Gibbs fundamental equation for an open system, $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i$ (Eq. 9.2.34), assumes the electric potential is zero. From this equation and Eq. 10.1.2, the Gibbs energy change during the transfer process at constant T and p is found to depend on ϕ according to

$$\mathrm{d}G(\phi) = [\mu_+(0) + z_+ F\phi]\,\mathrm{d}n_+ \tag{10.1.3}$$

The chemical potential of the cation in a phase of electric potential ϕ, defined by the partial molar Gibbs energy $[\partial G(\phi)/\partial n_+]_{T,p}$, is therefore given by

$$\mu_+(\phi) = \mu_+(0) + z_+ F\phi \tag{10.1.4}$$

The corresponding relation for an anion is

$$\mu_-(\phi) = \mu_-(0) + z_- F\phi \tag{10.1.5}$$

where z_- is the charge number of the anion (−1, −2, etc.). For a charged species in general, we have

$$\mu_i(\phi) = \mu_i(0) + z_i F\phi \tag{10.1.6}$$

We define the *standard state of an ion* on a molality basis in the same way as for a nonelectrolyte solute, with the additional stipulation that the ion is in a phase of zero electric potential. Thus, the standard state is a hypothetical state in which the ion is at molality m° with behavior extrapolated from infinite dilution on a molality basis, in a phase of pressure $p = p^\circ$ and electric potential ϕ=0.

The *standard chemical potential* μ_+° or μ_-° of a cation or anion is the chemical potential of the ion in its standard state. Single-ion activities a_+ and a_- in a phase of zero electric potential are defined by relations having the form of Eq. 9.7.8:

$$\mu_+(0) = \mu_+^\circ + RT\ln a_+ \qquad \mu_-(0) = \mu_-^\circ + RT\ln a_- \tag{10.1.7}$$

As explained in Sec. 9.7, a_+ and a_- should depend on the temperature, pressure, and composition of the phase, and not on the value of ϕ.

From Eqs. 10.1.4, 10.1.5, and 10.1.7, the relations between the chemical potential of a cation or anion, its activity, and the electric potential of its phase, are found to be

$$\mu_+ = \mu_+^\circ + RT \ln a_+ + z_+ F\phi \qquad \mu_- = \mu_-^\circ + RT \ln a_- + z_i F\phi \tag{10.1.8}$$

These relations are definitions of single-ion activities in a phase of electric potential ϕ.

For a charged species in general, we can write

$$\mu_i = \mu_i^\circ + RT \ln a_i + z_i F\phi \tag{10.1.9}$$

Note that we can also apply this equation to an uncharged species, because the charge number z_i is then zero and Eq. 10.1.9 becomes the same as Eq. 9.7.2.

> Some thermodynamicists call the quantity $(\mu_i^\circ + RT \ln a_i)$, which depends only on T, p, and composition, the *chemical potential* of ion i, and the quantity $(\mu_i^\circ + RT \ln a_i + z_i F\phi)$ the *electrochemical potential* with symbol $\tilde{\mu}_i$.

Of course there is no experimental way to evaluate either μ_+ or μ_- relative to a reference state or standard state, because it is impossible to add cations or anions by themselves to a solution. We can nevertheless write some theoretical relations involving μ_+ and μ_-.

For a given temperature and pressure, we can write the dependence of the chemical potentials of the ions on their molalities in the same form as that given by Eq. 9.5.18 for a nonelectrolyte solute:

$$\mu_+ = \mu_+^{\text{ref}} + RT \ln\left(\gamma_+ \frac{m_+}{m^\circ}\right) \qquad \mu_- = \mu_-^{\text{ref}} + RT \ln\left(\gamma_- \frac{m_-}{m^\circ}\right) \tag{10.1.10}$$

Here μ_+^{ref} and μ_-^{ref} are the chemical potentials of the cation and anion in solute reference states. Each reference state is defined as a hypothetical solution with the same temperature, pressure, and electric potential as the solution under consideration; in this solution, the molality of the ion has the standard value m°, and the ion behaves according to Henry's law based on molality. γ_+ and γ_- are single-ion activity coefficients on a molality basis.

The single-ion activity coefficients approach unity in the limit of infinite dilution:

$$\gamma_+ \to 1 \quad \text{and} \quad \gamma_- \to 1 \quad \text{as} \quad m_B \to 0 \qquad \begin{matrix}(10.1.11)\\ (\text{constant } T, p, \text{ and } \phi)\end{matrix}$$

In other words, we assume that in an extremely dilute electrolyte solution each individual ion behaves like a nonelectrolyte solute species in an ideal-dilute solution. At a finite solute molality, the values of γ_+ and γ_- are the ones that allow Eq. 10.1.10 to give the correct values of the quantities $(\mu_+ - \mu_+^{\text{ref}})$ and $(\mu_- - \mu_-^{\text{ref}})$. We have no way to actually measure these quantities experimentally, so we cannot evaluate either γ_+ or γ_-.

We can define single-ion pressure factors Γ_+ and Γ_- as follows:

$$\Gamma_+ \stackrel{\text{def}}{=} \exp\left(\frac{\mu_+^{\text{ref}} - \mu_+^\circ}{RT}\right) \approx \exp\left[\frac{V_+^\infty (p - p^\circ)}{RT}\right] \tag{10.1.12}$$

$$\Gamma_- \stackrel{\text{def}}{=} \exp\left(\frac{\mu_-^{\text{ref}} - \mu_-^\circ}{RT}\right) \approx \exp\left[\frac{V_-^\infty (p - p^\circ)}{RT}\right] \tag{10.1.13}$$

The approximations in these equations are like those in Table 9.6 for nonelectrolyte solutes; they are based on the assumption that the partial molar volumes V_+ and V_- are independent of pressure.

From Eqs. 10.1.7, 10.1.10, 10.1.12, and 10.1.13, the single-ion activities are related to the solution composition by

$$a_+ = \Gamma_+ \gamma_+ \frac{m_+}{m^\circ} \qquad a_- = \Gamma_- \gamma_- \frac{m_-}{m^\circ} \tag{10.1.14}$$

Then, from Eq. 10.1.9, we have the following relations between the chemical potentials and molalities of the ions:

$$\mu_+ = \mu_+^\circ + RT \ln(\Gamma_+ \gamma_+ m_+ / m^\circ) + z_+ F\phi \tag{10.1.15}$$

$$\mu_- = \mu_-^\circ + RT \ln(\Gamma_- \gamma_- m_- / m^\circ) + z_- F\phi \tag{10.1.16}$$

Like the values of γ_+ and γ_-, values of the single-ion quantities a_+, a_-, Γ_+, and Γ_- cannot be determined by experiment.

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5.8: Solution of a Symmetrical Electrolyte

Let us consider properties of an electrolyte solute as a whole. The simplest case is that of a binary solution in which the solute is a symmetrical strong electrolyte—a substance whose formula unit has one cation and one anion that dissociate completely. This condition will be indicated by $\nu = 2$, where ν is the number of ions per formula unit. In an aqueous solution, the solute with ν equal to 2 might be a 1:1 salt such as NaCl, a 2:2 salt such as $MgSO_4$, or a strong monoprotic acid such as HCl.

In this binary solution, the chemical potential of the solute as a whole is defined in the usual way as the partial molar Gibbs energy

$$\mu_B \overset{\text{def}}{=} \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} \tag{10.2.1}$$

and is a function of T, p, and the solute molality m_B. Although μ_B under given conditions must in principle have a definite value, we are not able to actually evaluate it because we have no way to measure precisely the energy brought into the system by the solute. This energy contributes to the internal energy and thus to G. We can, however, evaluate the differences $\mu_B - \mu_{m,B}^{\text{ref}}$ and $\mu_B - \mu_{m,B}^{\circ}$.

We can write the additivity rule (Eq. 9.2.25) for G as either

$$G = n_A\mu_A + n_B\mu_B \tag{10.2.2}$$

or

$$G = n_A\mu_A + n_+\mu_+ + n_-\mu_- \tag{10.2.3}$$

A comparison of these equations for a symmetrical electrolyte ($n_B = n_+ = n_-$) gives us the relation

$$\mu_B = \mu_+ + \mu_- \tag{10.2.4}$$
$$(\nu{=}2)$$

We see that the solute chemical potential in this case is the *sum* of the single-ion chemical potentials.

The solution is a phase of electric potential ϕ. From Eqs. 10.1.4 and 10.1.5, the sum $\mu_+ + \mu_-$ appearing in Eq. 10.2.4 is

$$\mu_+(\phi) + \mu_-(\phi) = \mu_+(0) + \mu_-(0) + (z_+ + z_-)F\phi \tag{10.2.5}$$

For the symmetrical electrolyte, the sum $(z_+ + z_-)$ is zero, so that μ_B is equal to $\mu_+(0) + \mu_-(0)$. We substitute the expressions of Eq. 10.1.10, use the relation $\mu_{m,B}^{\text{ref}} = \mu_+^{\text{ref}} + \mu_-^{\text{ref}}$ with reference states at ϕ=0, set the ion molalities m_+ and m_- equal to m_B, and obtain

$$\mu_B = \mu_{m,B}^{\text{ref}} + RT\ln\left[\gamma_+\gamma_-\left(\frac{m_B}{m^\circ}\right)^2\right] \tag{10.2.6}$$
$$(\nu{=}2)$$

The important feature of this relation is the appearance of the *second* power of m_B/m°, instead of the first power as in the case of a nonelectrolyte. Also note that μ_B does not depend on ϕ, unlike μ_+ and μ_-.

Although we cannot evaluate γ_+ or γ_- individually, we can evaluate the product $\gamma_+\gamma_-$. This product is the square of the **mean ionic activity coefficient** $\gamma_\pm$, defined for a symmetrical electrolyte by

$$\gamma_\pm \overset{\text{def}}{=} \sqrt{\gamma_+\gamma_-} \tag{10.2.7}$$
$$(\nu{=}2)$$

With this definition, Eq. 10.2.6 becomes

$$\mu_B = \mu_{m,B}^{\text{ref}} + RT\ln\left[(\gamma_\pm)^2\left(\frac{m_B}{m^\circ}\right)^2\right] \tag{10.2.8}$$
$$(\nu{=}2)$$

Since it is possible to determine the value of $\mu_B - \mu_{m,B}^{\text{ref}}$ for a solution of known molality, $\gamma_\pm$ is a measurable quantity.

> If the electrolyte (e.g., HCl) is sufficiently volatile, its mean ionic activity coefficient in a solution can be evaluated from partial pressure measurements of an equilibrated gas phase. Section 10.6 will describe a general method by which $\gamma_\pm$ can be found from osmotic coefficients. Section 14.5 describes how, in favorable cases, it is possible to evaluate $\gamma_\pm$ from the equilibrium cell potential of a galvanic cell.

The activity $a_{m,B}$ of a solute substance on a molality basis is defined by Eq. 9.7.8:

The activity $a_{m,\mathrm{B}}$ of a solute substance on a molality basis is defined by Eq. 9.7.8:

$$\mu_{\mathrm{B}} = \mu^{\circ}_{m,\mathrm{B}} + RT \ln a_{m,\mathrm{B}} \tag{10.2.9}$$

Here $\mu^{\circ}_{m,\mathrm{B}}$ is the chemical potential of the solute in its standard state, which is the solute reference state at the standard pressure. By equating the expressions for μ_{B} given by Eqs. 10.2.8 and 10.2.9 and solving for the activity, we obtain

$$a_{m,\mathrm{B}} = \Gamma_{m,\mathrm{B}} \, (\gamma_{\pm})^2 \left(\frac{m_{\mathrm{B}}}{m^{\circ}} \right)^2 \tag{10.2.10}$$
$$(\nu{=}2)$$

where $\Gamma_{m,\mathrm{B}}$ is the pressure factor defined by

$$\Gamma_{m,\mathrm{B}} \stackrel{\text{def}}{=} \exp \left(\frac{\mu^{\mathrm{ref}}_{m,\mathrm{B}} - \mu^{\circ}_{m,\mathrm{B}}}{RT} \right) \tag{10.2.11}$$

We can use the appropriate expression in Table 9.6 to evaluate $\Gamma_{m,\mathrm{B}}$ at an arbitrary pressure p':

$$\Gamma_{m,\mathrm{B}}(p') = \exp \left(\int_{p^{\circ}}^{p'} \frac{V^{\infty}_{\mathrm{B}}}{RT} \, \mathrm{d}p \right) \approx \exp \left[\frac{V^{\infty}_{\mathrm{B}}(p' - p^{\circ})}{RT} \right] \tag{10.2.12}$$

The value of $\Gamma_{m,\mathrm{B}}$ is $\mathbf{1}$ at the standard pressure, and close to $\mathbf{1}$ at any reasonably low pressure. For this reason it is common to see Eq. 10.2.10 written as $a_{m,\mathrm{B}} = \gamma_{\pm}^2 (m_{\mathrm{B}}/m^{\circ})^2$, with $\Gamma_{m,\mathrm{B}}$ omitted.

Equation 10.2.10 predicts that the activity of HCl in aqueous solutions is proportional, in the limit of infinite dilution, to the *square* of the HCl molality. In contrast, the activity of a *non*electrolyte solute is proportional to the *first* power of the molality in this limit. This predicted behavior of aqueous HCl is consistent with the data plotted in Fig. 10.1, and is confirmed by the data for dilute HCl solutions shown in Fig. 10.2(a). The dashed line in Fig. 10.2(a) is the extrapolation of the ideal-dilute behavior given by $a_{m,\mathrm{B}} = (m_{\mathrm{B}}/m^{\circ})^2$. The extension of this line to $m_{\mathrm{B}} = m^{\circ}$ establishes the hypothetical solute reference state based on molality, indicated by a filled circle in Fig. 10.2(b). (Since the data are for solutions at the standard pressure of $\mathbf{1\,bar}$, the solute reference state shown in the figure is also the solute standard state.)

The solid curve of Fig. 10.2(c) shows how the mean ionic activity coefficient of HCl varies with molality in approximately the same range of molalities as the data shown in Fig. 10.2(b). In the limit of infinite dilution, $\gamma_{\pm}$ approaches unity. The slope of the curve approaches $-\infty$ in this limit, quite unlike the behavior described in Sec. 9.5.4 for the activity coefficient of a nonelectrolyte solute.

For a symmetrical strong electrolyte, $\gamma_{\pm}$ is the geometric average of the single-ion activity coefficients γ_+ and γ_-. We have no way of evaluating γ_+ or γ_- individually, even if we know the value of $\gamma_{\pm}$. For instance, we cannot assume that γ_+ and γ_- are equal.

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5.9: Electrolytes in General

The formula unit of a *non*symmetrical electrolyte solute has more than two ions. General formulas for the solute as a whole are more complicated than those for the symmetrical case treated in the preceding section, but are derived by the same reasoning.

Again we assume the solute dissociates completely into its constituent ions. We define the following symbols:

$\nu_+ =$ the number of cations per solute formula unit

$\nu_- =$ the number of anions per solute formula unit

$\nu =$ the sum $\nu_+ + \nu_-$

For example, if the solute formula is $Al_2(SO_4)_3$, the values are ν_+=2, ν_-=3, and ν=5.

10.3.1 Solution of a single electrolyte

In a solution of a single electrolyte solute that is not necessarily symmetrical, the ion molalities are related to the overall solute molality by

$$m_+ = \nu_+ m_B \qquad m_- = \nu_- m_B \tag{10.3.1}$$

From the additivity rule for the Gibbs energy, we have

$$\begin{aligned} G &= n_A \mu_A + n_B \mu_B \\ &= n_A \mu_A + \nu_+ n_B \mu_+ + \nu_- n_B \mu_- \end{aligned} \tag{10.3.2}$$

giving the relation

$$\mu_B = \nu_+ \mu_+ + \nu_- \mu_- \tag{10.3.3}$$

in place of Eq. 10.2.4. The cations and anions are in the same phase of electric potential ϕ. We use Eqs. 10.1.4 and 10.1.5 to obtain

$$\nu_+ \mu_+(\phi) + \nu_- \mu_-(\phi) = \nu_+ \mu_+(0) + \nu_- \mu_-(0) + (\nu_+ z_+ + \nu_- z_-) F \phi \tag{10.3.4}$$

Electrical neutrality requires that $(\nu_+ z_+ + \nu_- z_-)$ be zero, giving

$$\mu_B = \nu_+ \mu_+(0) + \nu_- \mu_-(0) \tag{10.3.5}$$

By combining Eq. 10.3.5 with Eqs. 10.1.10, 10.3.1, and 10.3.3, we obtain

$$\mu_B = \mu_B^{\text{ref}} + RT \ln \left[\left(\nu_+^{\nu_+} \nu_-^{\nu_-} \right) \left(\gamma_+^{\nu_+} \right) \left(\gamma_-^{\nu_-} \right) \left(\frac{m_B}{m^\circ} \right)^\nu \right] \tag{10.3.6}$$

where $\mu_B^{\text{ref}} = \nu_+ \mu_+^{\text{ref}} + \nu_- \mu_-^{\text{ref}}$ is the chemical potential of the solute in the hypothetical reference state at ϕ=0 in which B is at the standard molality and behaves as at infinite dilution. Equation 10.3.6 is the generalization of Eq. 10.2.6. It shows that although μ_+ and μ_- depend on ϕ, μ_B does not.

The mean ionic activity coefficient $\gamma_\pm$ is defined in general by

$$\gamma_\pm^\nu = \left(\gamma_+^{\nu_+} \right) \left(\gamma_-^{\nu_-} \right) \tag{10.3.7}$$

or

$$\gamma_\pm = \left(\gamma_+^{\nu_+} \gamma_-^{\nu_-} \right)^{1/\nu} \tag{10.3.8}$$

Thus $\gamma_\pm$ is a geometric average of γ_+ and γ_- weighted by the numbers of the cations and anions in the solute formula unit. With a substitution from Eq. 10.3.7, Eq. 10.3.6 becomes

$$\mu_B = \mu_B^{\text{ref}} + RT \ln \left[\left(\nu_+^{\nu_+} \nu_-^{\nu_-} \right) \gamma_\pm^\nu \left(\frac{m_B}{m^\circ} \right)^\nu \right] \tag{10.3.9}$$

Since $\mu_B - \mu_B^{\text{ref}}$ is a measurable quantity, so also is $\gamma_\pm$.

The solute activity, defined by $\mu_B = \mu_{m,B}^\circ + RT \ln a_{m,B}$, is

$$a_{m,\mathrm{B}} = (\nu_+^{\nu_+}\nu_-^{\nu_-})\,\Gamma_{m,\mathrm{B}}\gamma_\pm^\nu\left(\frac{m_\mathrm{B}}{m^\circ}\right)^\nu \tag{10.3.10}$$

where $\Gamma_{m,\mathrm{B}}$ is the pressure factor that we can evaluate with Eq. 10.2.12. Equation 10.3.10 is the generalization of Eq. 10.2.10. From Eqs. 10.1.12, 10.1.13, and 10.2.11 and the relations $\mu_\mathrm{B}^\mathrm{ref} = \nu_+\mu_+^\mathrm{ref} + \nu_-\mu_-^\mathrm{ref}$ and $\mu_\mathrm{B}^\circ = \nu_+\mu_+^\circ + \nu_-\mu_-^\circ$, we obtain the relation

$$\Gamma_{m,\mathrm{B}} = \Gamma_+^{\nu_+}\Gamma_-^{\nu_-} \tag{10.3.11}$$

10.3.2 Multisolute solution

Equation 10.3.3 relates the chemical potential of electrolyte B in a binary solution to the single-ion chemical potentials of its constituent ions:

$$\mu_\mathrm{B} = \nu_+\mu_+ + \nu_-\mu_- \tag{10.3.12}$$

This relation is valid for each individual solute substance in a multisolute solution, even when two or more of the electrolyte solutes have an ion species in common.

As an illustration of this principle, consider a solution prepared by dissolving amounts n_B of $\mathrm{BaI_2}$ and n_C of CsI in an amount n_A of $\mathrm{H_2O}$. Assume the dissolved salts are completely dissociated into ions, with the $\mathrm{I^-}$ ion common to both. The additivity rule for the Gibbs energy of this solution can be written in the form

$$G = n_\mathrm{A}\mu_\mathrm{A} + n_\mathrm{B}\mu_\mathrm{B} + n_\mathrm{C}\mu_\mathrm{C} \tag{10.3.13}$$

and also, using single-ion quantities, in the form

$$G = n_\mathrm{A}\mu_\mathrm{A} + n_\mathrm{B}\mu(\mathrm{Ba^{2+}}) + 2n_\mathrm{B}\mu(\mathrm{I^-}) + n_\mathrm{C}\mu(\mathrm{Cs^+}) + n_\mathrm{C}\mu(\mathrm{I^-}) \tag{10.3.14}$$

Comparing Eqs. 10.3.13 and 10.3.14, we find the following relations must exist between the chemical potentials of the solute substances and the ion species:

$$\mu_\mathrm{B} = \mu(\mathrm{Ba^{2+}}) + 2\mu(\mathrm{I^-}) \qquad \mu_\mathrm{C} = \mu(\mathrm{Cs^+}) + \mu(\mathrm{I^-}) \tag{10.3.15}$$

These relations agree with Eq. 10.3.12. Note that $\mu(\mathrm{I^-})$, the chemical potential of the ion common to both salts, appears in both relations.

The solute activity $a_{m,\mathrm{B}}$ is defined by the relation $\mu_\mathrm{B} = \mu_\mathrm{B}^\circ + RT\ln a_{m,\mathrm{B}}$ (Eq. 10.2.9). Using this relation together with Eqs. 10.1.7 and 10.1.14, we find that the solute activity is related to ion molalities by

$$a_{m,\mathrm{B}} = \Gamma_{m,\mathrm{B}}\gamma_\pm^\nu\left(\frac{m_+}{m^\circ}\right)^{\nu_+}\left(\frac{m_-}{m^\circ}\right)^{\nu_-} \tag{10.3.16}$$

where the pressure factor $\Gamma_{m,\mathrm{B}}$ is defined in Eq. 10.2.11. The ion molalities in this expression refer to the constituent ions of solute B, which in a multisolute solution are not necessarily present in the same stoichiometric ratio as in the solute substance.

For instance, suppose we apply Eq. 10.3.16 to the solution of $\mathrm{BaI_2}$ and CsI used above as an illustration of a multisolute solution, letting $a_{m,\mathrm{B}}$ be the activity of solute substance $\mathrm{BaI_2}$. The quantities m_+ and m_- in the equation are then the molalities of the $\mathrm{Ba^{2+}}$ and $\mathrm{I^-}$ ions, and $\gamma_\pm$ is the mean ionic activity coefficient of the dissolved $\mathrm{BaI_2}$. Note that in this solution the $\mathrm{Ba^{2+}}$ and $\mathrm{I^-}$ ions are not present in the 1:2 ratio found in $\mathrm{BaI_2}$, because $\mathrm{I^-}$ is a constituent of both solutes.

10.3.3 Incomplete dissociation

In the preceding sections of this chapter, the electrolyte solute or solutes have been assumed to be completely dissociated into their constituent ions at all molalities. Some solutions, however, contain *ion pairs*—closely associated ions of opposite charge. Furthermore, in solutions of some electrolytes (often called “weak” electrolytes), an equilibrium is established between ions and electrically-neutral molecules. In these kinds of solutions, the relations between solute molality and ion molalities given by Eq. 10.3.1 are no longer valid. When dissociation is not complete, the expression for μ_B given by Eq. 10.3.9 can still be used. However, the quantity $\gamma_\pm$ appearing in the expression no longer has the physical significance of being the geometric average of the activity coefficients of the actual dissociated ions, and is called the **stoichiometric activity coefficient** of the electrolyte.

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5.10: The Debye-Hückel Theory

The theory of Peter Debye and Erich Hückel (1923) provides theoretical expressions for single-ion activity coefficients and mean ionic activity coefficients in electrolyte solutions. The expressions in one form or another are very useful for extrapolation of quantities that include mean ionic activity coefficients to low solute molality or infinite dilution.

The only interactions the theory considers are the electrostatic interactions between ions. These interactions are much stronger than those between uncharged molecules, and they die off more slowly with distance. If the positions of ions in an electrolyte solution were completely random, the net effect of electrostatic ion–ion interactions would be zero, because each cation–cation or anion–anion repulsion would be balanced by a cation–anion attraction. The positions are not random, however: each cation has a surplus of anions in its immediate environment, and each anion has a surplus of neighboring cations. Each ion therefore has a net attractive interaction with the surrounding ion atmosphere. The result for a cation species at low electrolyte molality is a decrease of μ_+ compared to the cation at same molality in the absence of ion–ion interactions, meaning that the single-ion activity coefficient γ_+ becomes less than **1** as the electrolyte molality is increased beyond the ideal-dilute range. Similarly, γ_- also becomes less than **1**.

According to the Debye–Hückel theory, the single-ion activity coefficient γ_i of ion i in a solution of one or more electrolytes is given by

$$\ln \gamma_i = -\frac{A_{\mathrm{DH}} z_i^2 \sqrt{I_m}}{1 + B_{\mathrm{DH}} a \sqrt{I_m}} \tag{10.4.1}$$

where

- The definitions of the quantities A_{DH} and B_{DH} appearing in Eq. 10.4.1 are

$$A_{\mathrm{DH}} \overset{\text{def}}{=} \left(N_{\mathrm{A}}^2 e^3 / 8\pi\right) \left(2\rho_{\mathrm{A}}^*\right)^{1/2} \left(\epsilon_{\mathrm{r}} \epsilon_0 RT\right)^{-3/2} \tag{10.4.3}$$

$$B_{\mathrm{DH}} \overset{\text{def}}{=} N_{\mathrm{A}} e \left(2\rho_{\mathrm{A}}^*\right)^{1/2} \left(\epsilon_{\mathrm{r}} \epsilon_0 RT\right)^{-1/2} \tag{10.4.4}$$

  where N_{A} is the Avogadro constant, e is the elementary charge (the charge of a proton), ρ_{A}^* and ϵ_{r} are the density and relative permittivity (dielectric constant) of the solvent, and ϵ_0 is the electric constant (or permittivity of vacuum).

  > Lewis and Randall (*J. Am. Chem. Soc.*, 1112–1154, 1921) introduced the term *ionic strength*, defined by Eq. 10.4.2, two years before the Debye–Hückel theory was published. They found empirically that in dilute solutions, the mean ionic activity coefficient of a given strong electrolyte is the same in all solutions having the same ionic strength.

  From Eqs. 10.3.8 and 10.4.1 and the electroneutrality condition $\nu_+ z_+ = \nu_- z_-$, we obtain the following expression for the logarithm of the mean ionic activity coefficient of an electrolyte solute:

$$\ln \gamma_\pm = -\frac{A_{\mathrm{DH}} |z_+ z_-| \sqrt{I_m}}{1 + B_{\mathrm{DH}} a \sqrt{I_m}} \tag{10.4.7}$$

  In this equation, z_+ and z_- are the charge numbers of the cation and anion of the solute. Since the right side of Eq. 10.4.7 is negative at finite solute molalities, and zero at infinite dilution, the theory predicts that $\gamma_\pm$ is less than **1** at finite solute molalities and approaches **1** at infinite dilution.

  Figure 10.4 shows $\ln \gamma_\pm$ as a function of $\sqrt{I_m}$ for aqueous HCl and $CaCl_2$. The experimental curves have the limiting slopes predicted by the Debye–Hückel limiting law (Eq. 10.4.8), but at a low ionic strength the curves begin to deviate significantly from the linear relations predicted by that law. The full Debye–Hückel equation (Eq. 10.4.7) fits the experimental curves over a wider range of ionic strength.

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5.11: The Gibbs Phase Rule for Multicomponent Systems

In Sec. 8.1.7, the Gibbs phase rule for a pure substance was written $F = 3 - P$. We now consider a system of more than one substance and more than one phase in an equilibrium state. The phase rule assumes the system is at thermal and mechanical equilibrium. We shall assume furthermore that in addition to the temperature and pressure, the only other state functions needed to describe the state are the amounts of the species in each phase; this means for instance that surface effects are ignored.

The derivations to follow will show that the phase rule may be written either in the form

$$F = 2 + C - P \tag{13.1.1}$$

or

$$F = 2 + s - r - P \tag{13.1.2}$$

where the symbols have the following meanings:

$F =$ the number of degrees of freedom (or variance)
$=$ the maximum number of intensive variables that can be varied independently while the system remains in an equilibrium state;

$C =$ the number of components
$=$ the minimum number of substances (or fixed-composition mixtures of substances) that could be used to prepare each phase individually;

$P =$ the number of different phases;

$s =$ the number of different species;

$r =$ the number of independent relations among intensive variables of individual phases other than relations needed for thermal, mechanical, and transfer equilibrium.

If we subdivide a phase, that does not change the number of phases P. That is, we treat noncontiguous regions of the system that have identical intensive properties as parts of the same phase.

Degrees of freedom

Consider a system in an equilibrium state. In this state, the system has one or more phases; each phase contains one or more species; and intensive properties such as T, p, and the mole fraction of a species in a phase have definite values. Starting with the system in this state, we can make changes that place the system in a new equilibrium state having the same kinds of phases and the same species, but different values of some of the intensive properties. The number of different independent intensive variables that we may change in this way is the **number of degrees of freedom** or **variance**, F, of the system.

Clearly, the system remains in equilibrium if we change the *amount* of a phase without changing its temperature, pressure, or composition. This, however, is the change of an extensive variable and is not counted as a degree of freedom.

The phase rule, in the form to be derived, applies to a system that continues to have complete thermal, mechanical, and transfer equilibrium as intensive variables change. This means different phases are not separated by adiabatic or rigid partitions, or by semipermeable or impermeable membranes. Furthermore, every conceivable reaction among the species is either at reaction equilibrium or else is frozen at a fixed advancement during the time period we observe the system.

The number of degrees of freedom is the maximum number of intensive properties of the equilibrium system we may independently vary, or fix at arbitrary values, without causing a change in the number and kinds of phases and species. We cannot, of course, change one of these properties to just any value whatever. We are able to vary the value only within a certain finite (sometimes quite narrow) range before a phase disappears or a new one appears.

The number of degrees of freedom is also the number of independent intensive variables needed to specify the equilibrium state in all necessary completeness, aside from the amount of each phase. In other words, when we specify values of F different independent intensive variables, then the values of all other intensive variables of the equilibrium state have definite values determined by the physical nature of the system.

Just as for a one-component system, we can use the terms *bivariant*, *univariant*, and *invariant* depending on the value of F (Sec. 8.1.7).

Species approach to the phase rule

This section derives an expression for the number of degrees of freedom, F, based on *species*. Section 13.1.3 derives an expression based on *components*. Both approaches yield equivalent versions of the phase rule.

Recall that a *species* is an entity, uncharged or charged, distinguished from other species by its chemical formula (Sec. 9.1.1). Thus, CO_2 and CO_3^{2-} are different species, but CO_2(aq) and CO_2(g) is the same species in different phases.

Consider an equilibrium system of P phases, each of which contains the same set of species. Let the number of different species be s. If we could make changes while the system remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we could independently vary the temperature and pressure of the system as a whole and the amount of each species in each phase; there would then be $2 + Ps$ independent variables.

The equilibrium system is, however, in transfer equilibrium, which requires each species to have the same chemical potential in each phase: $\mu_i^\beta = \mu_i^\alpha$, $\mu_i^\gamma = \mu_i^\alpha$, and so on. There are $P - 1$ independent relations like this for each species, and a total of $s(P - 1)$ independent relations for all species. Each such independent relation introduces a constraint and reduces the number of independent variables by one. Accordingly, taking transfer equilibrium into account, the number of independent variables is $2 + Ps - s(P - 1) = 2 + s$.

We obtain the same result if a species present in one phase is totally excluded from another. For example, solvent molecules of a solution are not found in a pure perfectly-ordered crystal of the solute, undissociated molecules of a volatile strong acid such as HCl can exist in a gas phase but not in aqueous solution, and ions of an electrolyte solute are usually not found in a gas phase. For each such species absent from a phase, there is one fewer amount variable and also one fewer relation for transfer equilibrium; on balance, the number of independent variables is still $2 + s$.

Next, we consider the possibility that further independent relations exist among intensive variables in addition to the relations needed for thermal, mechanical, and transfer equilibrium. (Relations such as $\sum_i p_i = p$ for a gas phase or $\sum_i x_i = 1$ for a phase in general have already been accounted for in the derivation by the specification of p and the amount of each species.) If there are r of these additional relations, the total number of independent variables is reduced to $2 + s - r$. These relations may come from

1. In the case of a reaction equilibrium, the relation is $\Delta_r G = \sum_i \nu_i \mu_i = 0$, or the equivalent relation $K = \prod_i (a_i)^{\nu_i}$ for the thermodynamic equilibrium constant. Thus, r is the sum of the number of independent reaction equilibria, the number of phases containing ions, and the number of independent initial conditions. Several examples will be given in Sec. 13.1.4.

   There is an infinite variety of possible choices of the independent variables (both extensive and intensive) for the equilibrium system, but the total *number* of independent variables is fixed at $2 + s - r$. Keeping intensive properties fixed, we can always vary how much of each phase is present (e.g., its volume, mass, or amount) without destroying the equilibrium. Thus, at least P of the independent variables, one for each phase, must be extensive. It follows that the maximum number of independent *intensive* variables is the difference $(2 + s - r) - P$.

   Since the maximum number of independent intensive variables is the number of degrees of freedom, our expression for F based on species is

$$F = 2 + s - r - P \tag{13.1.3}$$

Components approach to the phase rule

The derivation of the phase rule in this section uses the concept of **components**. The number of components, C, is the minimum number of substances or mixtures of fixed composition from which we could in principle prepare each individual phase of an equilibrium state of the system, using methods that may be hypothetical. These methods include the addition or removal of one or more of the substances or fixed-composition mixtures, and the conversion of some of the substances into others by means of a reaction that is at equilibrium in the actual system.

It is not always easy to decide on the number of components of an equilibrium system. The number of components may be less than the number of substances present, on account of the existence of reaction equilibria that produce some substances from

others. When we use a reaction to prepare a phase, nothing must remain unused. For instance, consider a system consisting of solid phases of $CaCO_3$ and CaO and a gas phase of CO_2. Assume the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ is at equilibrium. We could prepare the $CaCO_3$ phase from CaO and CO_2 by the reverse of this reaction, but we can only prepare the CaO and CO_2 phases from the individual substances. We could not use $CaCO_3$ to prepare either the CaO phase or the CO_2 phase, because CO_2 or CaO would be left over. Thus this system has three substances but only two components, namely CaO and CO_2.

In deriving the phase rule by the components approach, it is convenient to consider only intensive variables. Suppose we have a system of P phases in which each substance present is a component (i.e., there are no reactions) and each of the C components is present in each phase. If we make changes to the system while it remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we can independently vary the temperature and pressure of the whole system, and for each phase we can independently vary the mole fraction of all but one of the substances (the value of the omitted mole fraction comes from the relation $\sum_i x_i = 1$). This is a total of $2 + P(C-1)$ independent intensive variables.

When there also exist transfer and reaction equilibria, not all of these variables are independent. Each substance in the system is either a component, or else can be formed from components by a reaction that is in reaction equilibrium in the system. Transfer equilibria establish $P-1$ independent relations for each component ($\mu_i^\beta = \mu_i^\alpha$, $\mu_i^\gamma = \mu_i^\alpha$, etc.) and a total of $C(P-1)$ relations for all components. Since these are relations among chemical potentials, which are intensive properties, each relation reduces the number of independent intensive variables by one. The resulting number of independent intensive variables is

$$F = [2 + P(C-1)] - C(P-1) = 2 + C - P \tag{13.1.4}$$

If the equilibrium system lacks a particular component in one phase, there is one fewer mole fraction variable and one fewer relation for transfer equilibrium. These changes cancel in the calculation of F, which is still equal to $2 + C - P$. If a phase contains a substance that is formed from components by a reaction, there is an additional mole fraction variable and also the additional relation $\sum_i \nu_i \mu_i = 0$ for the reaction; again the changes cancel.

> We may need to *remove* a component from a phase to achieve the final composition. Note that it is not necessary to consider additional relations for electroneutrality or initial conditions; they are implicit in the definitions of the components. For instance, since each component is a substance of zero electric charge, the electrical neutrality of the phase is assured.

We conclude that, regardless of the kind of system, the expression for F based on components is given by $F = 2 + C - P$. By comparing this expression and $F = 2 + s - r - P$, we see that the number of components is related to the number of species by

$$C = s - r \tag{13.1.5}$$

Examples

The five examples below illustrate various aspects of using the phase rule.

Example 1: liquid water

For a single phase of pure water, P equals 1. If we treat the water as the single species H_2O, s is 1 and r is 0. The phase rule then predicts two degrees of freedom:

$$\begin{aligned} F &= 2 + s - r - P \\ &= 2 + 1 - 0 - 1 = 2 \end{aligned} \tag{13.1.6}$$

Since F is the number of intensive variables that can be varied independently, we could for instance vary T and p independently, or T and ρ, or any other pair of independent intensive variables.

Next let us take into account the proton transfer equilibrium

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{5.11.1}$$

and consider the system to contain the three species H_2O, H_3O^+, and OH^-. Then for the species approach to the phase rule, we have $s = 3$. We can write two independent relations:

1. Thus, we have two relations involving intensive variables only. Now s is 3, r is 2, P is 1, and the number of degrees of freedom is given by

$$F = 2 + s - r - P = 2 \tag{13.1.7}$$

which is the same value of F as before.

If we consider water to contain additional cation species (e.g., $H_5O_2^+$), each such species would add 1 to s and 1 to r, but F would remain equal to 2. Thus, no matter how complicated are the equilibria that actually exist in liquid water, the number of degrees of freedom remains 2.

Example 2: carbon, oxygen, and carbon oxides

Consider a system containing solid carbon (graphite) and a gaseous mixture of O_2, CO, and CO_2. There are four species and two phases. If reaction equilibrium is absent, as might be the case at low temperature in the absence of a catalyst, we have $r = 0$ and $C = s - r = 4$. The four components are the four substances. The phase rule tells us the system has four degrees of freedom. We could, for instance, arbitrarily vary T, p, y_{O_2}, and y_{CO}.

Now suppose we raise the temperature or introduce an appropriate catalyst to allow the following reaction equilibria to exist:

1. These equilibria introduce two new independent relations among chemical potentials and among activities. We could also consider the equilibrium $2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$, but it does not contribute an additional independent relation because it depends on the other two equilibria: the reaction equation is obtained by subtracting the reaction equation for equilibrium 1 from twice the reaction equation for equilibrium 2. By the species approach, we have $s = 4$, $r = 2$, and $P = 2$; the number of degrees of freedom from these values is

$$F = 2 + s - r - P = 2 \tag{13.1.8}$$

If we wish to calculate F by the components approach, we must decide on the minimum number of substances we could use to prepare each phase separately. (This does not refer to how we actually prepare the two-phase system, but to a hypothetical preparation of each phase with any of the compositions that can actually exist in the equilibrium system.) Assume equilibria 1 and 2 are present. We prepare the solid phase with carbon, and we can prepare any possible equilibrium composition of the gas phase from carbon and O_2 by using the reactions of both equilibria. Thus, there are two components (C and O_2) giving the same result of two degrees of freedom.

1. Now to introduce an additional complexity: Suppose we prepare the system by placing a certain amount of O_2 and twice this amount of carbon in an evacuated container, and wait for the reactions to come to equilibrium. This method of preparation imposes an initial condition on the system, and we must decide whether the number of degrees of freedom is affected. Equating the total amount of carbon atoms to the total amount of oxygen atoms in the equilibrated system gives the relation

$$n_C + n_{CO} + n_{CO_2} = 2n_{O_2} + n_{CO} + 2n_{CO_2} \qquad \text{or} \qquad n_C = 2n_{O_2} + n_{CO_2} \tag{13.1.9}$$

Either equation is a relation among extensive variables of the two phases. From them, we are unable to obtain any relation among *intensive* variables of the phases. Therefore, this particular initial condition does not change the value of r, and F remains equal to 2.

Example 3: a solid salt and saturated aqueous solution

Applying the components approach to this system is straightforward. The solid phase is prepared from $PbCl_2$ and the aqueous phase could be prepared by dissolving solid $PbCl_2$ in H_2O. Thus, there are two components and two phases:

$$F = 2 + C - P = 2 \tag{13.1.10}$$

For the species approach, we note that there are four species ($PbCl_2$, Pb^{2+}, Cl^-, and H_2O) and two independent relations among intensive variables:

1. We have $s = 4$, $r = 2$, and $P = 2$, giving the same result as the components approach:

$$F = 2 + s - r - P = 2 \tag{13.1.11}$$

Example 4: liquid water and water-saturated air

If there is no special relation among the total amounts of N_2 and O_2, there are three components and the phase rule gives

$$F = 2 + C - P = 3 \tag{13.1.12}$$

Since there are three degrees of freedom, we could, for instance, specify arbitrary values of T, p, and y_{N_2} (arbitrary, that is, within the limits that would allow the two phases to coexist); then the values of other intensive variables such as the mole fractions y_{H_2O} and x_{N_2} would have definite values.

Now suppose we impose an initial condition by preparing the system with water and dry air of a *fixed* composition. The mole ratio of N_2 and O_2 in the aqueous solution is not necessarily the same as in the equilibrated gas phase; consequently, the air does not behave like a single substance. The number of components is still three: H_2O, N_2, and O_2 are all required to prepare each phase individually, just as when there was no initial condition, giving $F = 3$ as before.

The fact that the compositions of both phases depend on the relative amounts of the phases is illustrated in Prob. 9.5.

We can reach the same conclusion with the species approach. The initial condition can be expressed by an equation such as

$$\frac{(n^l_{N_2} + n^g_{N_2})}{(n^l_{O_2} + n^g_{O_2})} = a \tag{13.1.13}$$

where a is a constant equal to the mole ratio of N_2 and O_2 in the dry air. This equation cannot be changed to a relation between intensive variables such as x_{N_2} and x_{O_2}, so that r is zero and there are still three degrees of freedom.

Finally, let us assume that we prepare the system with dry air of fixed composition, as before, but consider the solubilities of N_2 and O_2 in water to be negligible. Then $n^l_{N_2}$ and $n^l_{O_2}$ are zero and Eq. 13.1.13 becomes $n^g_{N_2}/n^g_{O_2} = a$, or $y_{N_2} = a y_{O_2}$, which is a relation between intensive variables. In this case, r is 1 and the phase rule becomes

$$F = 2 + s - r - P = 2 \tag{13.1.14}$$

The reduction in the value of F from 3 to 2 is a consequence of our inability to detect any dissolved N_2 or O_2. According to the components approach, we may prepare the liquid phase with H_2O and the gas phase with H_2O and air of fixed composition that behaves as a single substance; thus, there are only two components.

Example 5: equilibrium between two solid phases and a gas phase

Consider the following reaction equilibrium:

$$3\,CuO(s) + 2\,NH_3(g) \rightleftharpoons 3\,Cu(s) + 3\,H_2O(g) + N_2(g) \tag{5.11.2}$$

According to the species approach, there are five species, one relation (for reaction equilibrium), and three phases. The phase rule gives

$$F = 2 + s - r - P = 3 \tag{13.1.15}$$

It is more difficult to apply the components approach to this example. As components, we might choose CuO and Cu (from which we could prepare the solid phases) and also NH_3 and H_2O. Then to obtain the N_2 needed to prepare the gas phase, we could use CuO and NH_3 as reactants in the reaction $3\,CuO + 2\,NH_3 \rightarrow 3\,Cu + 3\,H_2O + N_2$ and remove the products Cu and H_2O. In the components approach, we are allowed to remove substances from the system provided they are counted as components.

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5.12: Phase Diagrams- Binary Systems

As explained in Sec. 8.2, a phase diagram is a kind of two-dimensional map that shows which phase or phases are stable under a given set of conditions. This section discusses some common kinds of binary systems, and Sec. 13.3 will describe some interesting ternary systems.

Generalities

A binary system has two components; C equals 2, and the number of degrees of freedom is $F = 4 - P$. There must be at least one phase, so the maximum possible value of F is 3. Since F cannot be negative, the equilibrium system can have no more than four phases.

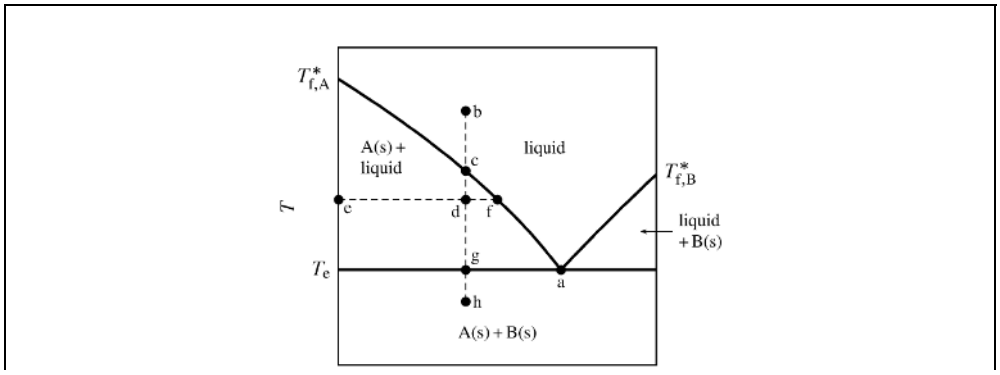
We can independently vary the temperature, pressure, and composition of the system as a whole. Instead of using these variables as the coordinates of a three-dimensional phase diagram, we usually draw a two-dimensional phase diagram that is either a temperature–composition diagram at a fixed pressure or a pressure–composition diagram at a fixed temperature. The position of the system point on one of these diagrams then corresponds to a definite temperature, pressure, and overall composition. The composition variable usually varies along the horizontal axis and can be the mole fraction, mass fraction, or mass percent of one of the components, as will presently be illustrated by various examples.

The way in which we interpret a two-dimensional phase diagram to obtain the compositions of individual phases depends on the number of phases present in the system.

- If the system point falls within a *one-phase* area of the phase diagram, the composition variable is the composition of that single phase. There are three degrees of freedom. On the phase diagram, the value of either T or p has been fixed, so there are two other independent intensive variables. For example, on a temperature–composition phase diagram, the pressure is fixed and the temperature and composition can be changed independently within the boundaries of the one-phase area of the diagram.
- If the system point is in a *two-phase* area of the phase diagram, we draw a horizontal *tie line* of constant temperature (on a temperature–composition phase diagram) or constant pressure (on a pressure–composition phase diagram). The lever rule applies. The position of the point at each end of the tie line, at the boundary of the two-phase area, gives the value of the composition variable of one of the phases and also the physical state of this phase: either the state of an adjacent one-phase area, or the state of a phase of fixed composition when the boundary is a vertical line. Thus, a boundary that separates a two-phase area for phases α and β from a one-phase area for phase α is a curve that describes the composition of phase α as a function of T or p when it is in equilibrium with phase β. The curve is called a *solidus*, *liquidus*, or *vaporus* depending on whether phase α is a solid, liquid, or gas.
- A binary system with *three* phases has only one degree of freedom and cannot be represented by an area on a two-dimensional phase diagram. Instead, there is a horizontal boundary line between areas, with a special point along the line at the junction of several areas. The compositions of the three phases are given by the positions of this point and the points at the two ends of the line. The position of the system point on this line does not uniquely specify the relative amounts in the three phases.

The examples that follow show some of the simpler kinds of phase diagrams known for binary systems.

Solid–liquid systems



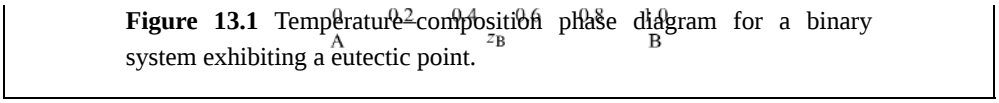


Figure 13.1 Temperature–composition phase diagram for a binary system exhibiting a eutectic point.

Figure 13.1 is a temperature–composition phase diagram at a fixed pressure. The composition variable z_B is the mole fraction of component B in the system as a whole. The phases shown are a binary liquid mixture of A and B, pure solid A, and pure solid B.

The one-phase liquid area is bounded by two curves, which we can think of either as freezing-point curves for the liquid or as solubility curves for the solids. These curves comprise the liquidus. As the mole fraction of either component in the liquid phase decreases from unity, the freezing point decreases. The curves meet at point a, which is a **eutectic point**. At this point, both solid A and solid B can coexist in equilibrium with a binary liquid mixture. The composition at this point is the *eutectic composition*, and the temperature here (denoted T_e) is the *eutectic temperature*. ("Eutectic" comes from the Greek for *easy melting*.) T_e is the lowest temperature for the given pressure at which the liquid phase is stable.

Suppose we combine $0.60\,\text{mol}$ A and $0.40\,\text{mol}$ B ($z_B = 0.40$) and adjust the temperature so as to put the system point at b. This point is in the one-phase liquid area, so the equilibrium system at this temperature has a single liquid phase. If we now place the system in thermal contact with a cold reservoir, heat is transferred out of the system and the system point moves down along the *isopleth* (path of constant overall composition) b–h. The cooling rate depends on the temperature gradient at the system boundary and the system's heat capacity.

At point c on the isopleth, the system point reaches the boundary of the one-phase area and is about to enter the two-phase area labeled A(s) + liquid. At this point in the cooling process, the liquid is saturated with respect to solid A, and solid A is about to freeze out from the liquid. There is an abrupt decrease (break) in the cooling rate at this point, because the freezing process involves an extra enthalpy decrease.

At the still lower temperature at point d, the system point is within the two-phase solid–liquid area. The tie line through this point is line e–f. The compositions of the two phases are given by the values of z_B at the ends of the tie line: $x_B^s = 0$ for the solid and $x_B^l = 0.50$ for the liquid. From the general lever rule (Eq. 8.2.8), the ratio of the amounts in these phases is

$$\frac{n^l}{n^s} = \frac{z_B - x_B^s}{x_B^l - z_B} = \frac{0.40 - 0}{0.50 - 0.40} = 4.0 \tag{13.2.1}$$

Since the total amount is $n^s + n^l = 1.00\,\text{mol}$, the amounts of the two phases must be $n^s = 0.20\,\text{mol}$ and $n^l = 0.80\,\text{mol}$.

When the system point reaches the eutectic temperature at point g, cooling halts until all of the liquid freezes. Solid B freezes out as well as solid A. During this *eutectic halt*, there are at first three phases: liquid with the eutectic composition, solid A, and solid B. As heat continues to be withdrawn from the system, the amount of liquid decreases and the amounts of the solids increase until finally only $0.60\,\text{mol}$ of solid A and $0.40\,\text{mol}$ of solid B are present. The temperature then begins to decrease again and the system point enters the two-phase area for solid A and solid B; tie lines in this area extend from z_B=0 to z_B=1.

Temperature–composition phase diagrams such as this are often mapped out experimentally by observing the cooling curve (temperature as a function of time) along isopleths of various compositions. This procedure is *thermal analysis*. A break in the slope of a cooling curve at a particular temperature indicates the system point has moved from a one-phase liquid area to a two-phase area of liquid and solid. A temperature halt indicates the temperature is either the freezing point of the liquid to form a solid of the same composition, or else a eutectic temperature.

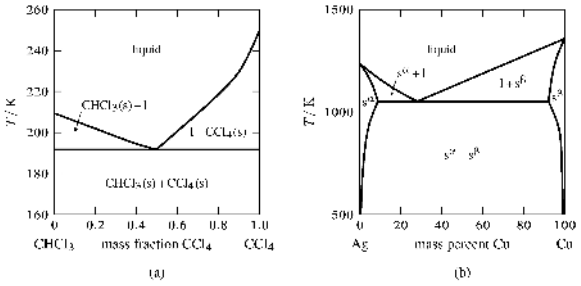


Figure 13.2 Temperature–composition phase diagrams with single eutectics.
(a) Two pure solids and a liquid mixture (E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. IV, McGraw-Hill, New York, 1928, p. 98).
(b) Two solid solutions and a liquid mixture.

Figure 13.2 shows two temperature–composition phase diagrams with single eutectic points. The left-hand diagram is for the binary system of chloroform and carbon tetrachloride, two liquids that form nearly ideal mixtures. The solid phases are pure crystals, as in Fig. 13.1. The right-hand diagram is for the silver–copper system and involves solid phases that are solid solutions (substitutional alloys of variable composition). The area labeled s^{α} is a solid solution that is mostly silver, and s^{β} is a solid solution that is mostly copper. Tie lines in the two-phase areas do not end at a vertical line for a pure solid component as they do in the system shown in the left-hand diagram. The three phases that can coexist at the eutectic temperature of $1{,}052\,\mathrm{K}$ are the melt of the eutectic composition and the two solid solutions.

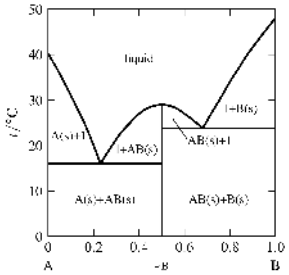


Figure 13.3 Temperature–composition phase diagram for the binary system of α-naphthylamine (A) and phenol (B) at $1\,\mathrm{bar}$ (J. C. Philip, *J. Chem. Soc.*, **83**, 814–834, 1903).

Section 12.5.4 discussed the possibility of the appearance of a *solid compound* when a binary liquid mixture is cooled. An example of this behavior is shown in Fig. 13.3, in which the solid compound contains equal amounts of the two components α-naphthylamine and phenol. The possible solid phases are pure A, pure B, and the solid compound AB. Only one or two of these solids can be present simultaneously in an equilibrium state. The vertical line in the figure at $z_{\mathrm{B}} = 0.5$ represents the solid compound. The temperature at the upper end of this line is the melting point of the solid compound, $29\,^{\circ}\mathrm{C}$. The solid melts *congruently* to give a liquid of the same composition. A melting process with this behavior is called a *dystectic reaction*. The cooling curve for liquid of this composition would display a halt at the melting point.

The phase diagram in Fig. 13.3 has two eutectic points. It resembles two simple phase diagrams like Fig. 13.1 placed side by side. There is one important difference: the slope of the freezing-point curve (liquidus curve) is nonzero at the composition of a pure component, but is zero at the composition of a solid compound that is completely dissociated in the liquid (as derived theoretically in Sec. 12.5.4). Thus, the curve in Fig. 13.3 has a relative maximum at the composition of the solid compound ($z_B = 0.5$) and is rounded there, instead of having a cusp—like a Romanesque arch rather than a Gothic arch.

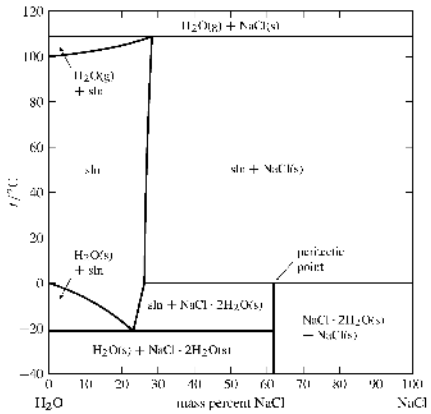


Figure 13.4 Temperature–composition phase diagram for the binary system of H_2O and NaCl at $\mathbf{1\,bar}$. (Data from Roger Cohen-Adad and John W. Lorimer, *Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems)*, Solubility Data Series, Vol. 47, Pergamon Press, Oxford, 1991; and E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. III, McGraw-Hill, New York, 1928.)

An example of a solid compound that does not melt congruently is shown in Fig. 13.4. The solid hydrate $\mathbf{NaCl \cdot 2\,H_2O}$ is $\mathbf{61.9\%}$ NaCl by mass. It decomposes at $\mathbf{0\,°C}$ to form an aqueous solution of composition $\mathbf{26.3\%}$ NaCl by mass and a solid phase of anhydrous NaCl. These three phases can coexist at equilibrium at $\mathbf{0\,°C}$. A phase transition like this, in which a solid compound changes into a liquid and a different solid, is called *incongruent* or *peritectic* melting, and the point on the phase diagram at this temperature at the composition of the liquid is a *peritectic point*.

Figure 13.4 shows there are two other temperatures at which three phases can be present simultaneously: $\mathbf{-21\,°C}$, where the phases are ice, the solution at its eutectic point, and the solid hydrate; and $\mathbf{109\,°C}$, where the phases are gaseous H_2O, a solution of composition $\mathbf{28.3\%}$ NaCl by mass, and solid NaCl. Note that both segments of the right-hand boundary of the one-phase solution area have positive slopes, meaning that the solubilities of the solid hydrate and the anhydrous salt both increase with increasing temperature.

Partially-miscible liquids

When two liquids that are partially miscible are combined in certain proportions, phase separation occurs (Sec. 11.1.6). Two liquid phases in equilibrium with one another are called *conjugate phases*. Obviously the two phases must have different compositions or they would be identical; the difference is called a *miscibility gap*. A binary system with two phases has two degrees of freedom, so that at a given temperature and pressure each conjugate phase has a fixed composition.

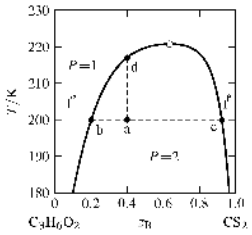


Figure 13.5 Temperature–composition phase diagram for the binary system of methyl acetate (A) and carbon disulfide (B) at **1 bar** (data from P. Ferloni and G. Spinolo, *Int. DATA Ser., Sel. Data Mixtures, Ser. A*, 70, 1974). All phases are liquids. The open circle indicates the critical point.

The typical dependence of a miscibility gap on temperature is shown in Fig. 13.5. The miscibility gap (the difference in compositions at the left and right boundaries of the two-phase area) decreases as the temperature increases until at the *upper consolute temperature*, also called the *upper critical solution temperature*, the gap vanishes. The point at the maximum of the boundary curve of the two-phase area, where the temperature is the upper consolute temperature, is the *consolute point* or *critical point*. At this point, the two liquid phases become identical, just as the liquid and gas phases become identical at the critical point of a pure substance. Critical opalescence (Sec. 8.2.3) is observed in the vicinity of this point, caused by large local composition fluctuations. At temperatures at and above the critical point, the system is a single binary liquid mixture.

Suppose we combine $6.0\,\mathrm{mol}$ of component A (methyl acetate) and $4.0\,\mathrm{mol}$ of component B (carbon disulfide) in a cylindrical vessel and adjust the temperature to $200\,\mathrm{K}$. The overall mole fraction of B is $z_\mathrm{B} = 0.40$. The system point is at point a in the two-phase region. From the positions of points b and c at the ends of the tie line through point a, we find the two liquid layers have compositions $x_\mathrm{B}^\alpha = 0.20$ and $x_\mathrm{B}^\beta = 0.92$. Since carbon disulfide is the more dense of the two pure liquids, the bottom layer is phase β, the layer that is richer in carbon disulfide. According to the lever rule, the ratio of the amounts in the two phases is given by

$$\frac{n^\beta}{n^\alpha} = \frac{z_\mathrm{B} - x_\mathrm{B}^\alpha}{x_\mathrm{B}^\beta - z_\mathrm{B}} = \frac{0.40 - 0.20}{0.92 - 0.40} = 0.38 \qquad (13.2.2)$$

Combining this value with $n^\alpha + n^\beta = 10.0\,\mathrm{mol}$ gives us $n^\alpha = 7.2\,\mathrm{mol}$ and $n^\beta = 2.8\,\mathrm{mol}$.

If we gradually add more carbon disulfide to the vessel while gently stirring and keeping the temperature constant, the system point moves to the right along the tie line. Since the ends of this tie line have fixed positions, neither phase changes its composition, but the amount of phase β increases at the expense of phase α. The liquid–liquid interface moves up in the vessel toward the top of the liquid column until, at overall composition $z_\mathrm{B} = 0.92$ (point c), there is only one liquid phase.

Now suppose the system point is back at point a and we raise the temperature while keeping the overall composition constant at $z_\mathrm{B} = 0.40$. The system point moves up the isopleth a–d. The phase diagram shows that the ratio $(z_\mathrm{B} - x_\mathrm{B}^\alpha)/(x_\mathrm{B}^\beta - z_\mathrm{B})$ decreases during this change. As a result, the amount of phase α increases, the amount of phase β decreases, and the liquid–liquid interface moves down toward the bottom of the vessel until at $217\,\mathrm{K}$ (point d) there again is only one liquid phase.

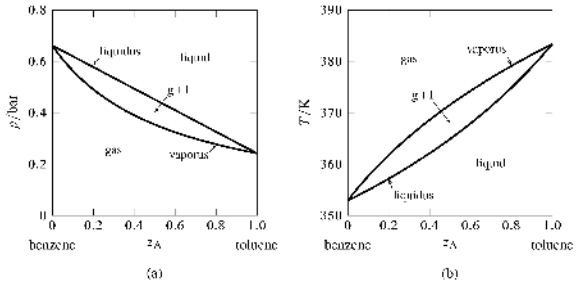


Figure 13.6 Phase diagrams for the binary system of toluene (A) and benzene (B). The curves are calculated from Eqs. 13.2.6 and 13.2.7 and the saturation vapor pressures of the pure liquids.
(a) Pressure–composition diagram at $T = 340\,\mathrm{K}$.
(b) Temperature–composition diagram at $p = 1\,\mathrm{bar}$.

Toluene and benzene form liquid mixtures that are practically ideal and closely obey Raoult's law for partial pressure. For the binary system of these components, we can use the vapor pressures of the pure liquids to generate the liquidus and vaporus curves of the pressure–composition and temperature–composition phase diagram. The results are shown in Fig. 13.6. The composition variable z_A is the overall mole fraction of component A (toluene).

The equations needed to generate the curves can be derived as follows. Consider a binary liquid mixture of components A and B and mole fraction composition x_A that obeys Raoult's law for partial pressure (Eq. 9.4.2):

$$p_A = x_A p_A^* \qquad p_B = (1 - x_A) p_B^* \tag{13.2.3}$$

Strictly speaking, Raoult's law applies to a liquid–gas system maintained at a constant pressure by means of a third gaseous component, and p_A^* and p_B^* are the vapor pressures of the pure liquid components at this pressure and the temperature of the system. However, when a liquid phase is equilibrated with a gas phase, the partial pressure of a constituent of the liquid is practically independent of the total pressure (Sec. 12.8.1), so that it is a good approximation to apply the equations to a *binary* liquid–gas system and treat p_A^* and p_B^* as functions only of T.

When the binary system contains a liquid phase and a gas phase in equilibrium, the pressure is the sum of p_A and p_B, which from Eq. 13.2.3 is given by

$$\begin{aligned} p &= x_A p_A^* + (1 - x_A) p_B^* \\ &= p_B^* + (p_A^* - p_B^*) x_A \end{aligned} \qquad \begin{matrix} (13.2.4) \\ (C{=}2,\ \text{ideal liquid mixture}) \end{matrix}$$

where x_A is the mole fraction of A in the liquid phase. Equation 13.2.4 shows that in the two-phase system, p has a value between p_A^* and p_B^*, and that if T is constant, p is a linear function of x_A. The mole fraction composition of the gas in the two-phase system is given by

$$y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} \tag{13.2.5}$$

A binary two-phase system has two degrees of freedom. At a given T and p, each phase must have a fixed composition. We can calculate the liquid composition by rearranging Eq. 13.2.4:

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*} \qquad \begin{matrix} (13.2.6) \\ (C{=}2,\ \text{ideal liquid mixture}) \end{matrix}$$

The gas composition is then given by

$$y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{p} = \left(\frac{p - p_B^*}{p_A^* - p_B^*}\right)\frac{p_A^*}{p} \qquad (C{=}2,\ \text{ideal liquid mixture}) \tag{13.2.7}$$

If we know p_A^* and p_B^* as functions of T, we can use Eqs. 13.2.6 and 13.2.7 to calculate the compositions for any combination of T and p at which the liquid and gas phases can coexist, and thus construct a pressure–composition or temperature–composition phase diagram.

In Fig. 13.6(a), the liquidus curve shows the relation between p and x_A for equilibrated liquid and gas phases at constant T, and the vaporus curve shows the relation between p and y_A under these conditions. We see that p is a linear function of x_A but not of y_A.

In a similar fashion, the liquidus curve in Fig. 13.6(b) shows the relation between T and x_A, and the vaporus curve shows the relation between T and y_A, for equilibrated liquid and gas phases at constant p. Neither curve is linear.

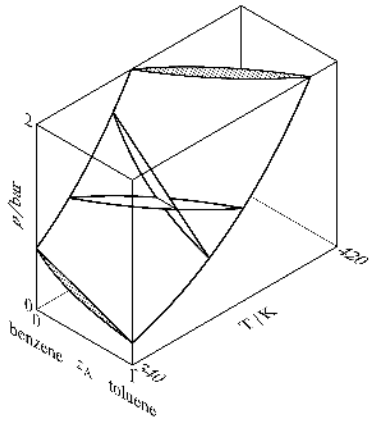


Figure 13.7 Liquidus and vaporus surfaces for the binary system of toluene (A) and benzene. Cross-sections through the two-phase region are drawn at constant temperatures of 340 K and 370 K and at constant pressures of 1 bar and 2 bar. Two of the cross-sections intersect at a tie line at $T = 370\,\text{K}$ and $p = 1\,\text{bar}$, and the other cross-sections are hatched in the direction of the tie lines.

A liquidus curve is also called a *bubble-point* curve or a *boiling-point* curve. Other names for a vaporus curve are *dew-point* curve and *condensation* curve. These curves are actually cross-sections of liquidus and vaporus *surfaces* in a three-dimensional T–p–z_A phase diagram, as shown in Fig. 13.7. In this figure, the liquidus surface is in view at the front and the vaporus surface is hidden behind it.

Liquid–gas systems with nonideal liquid mixtures

Most binary liquid mixtures do not behave ideally. The most common situation is *positive* deviations from Raoult's law. (In the molecular model of Sec. 11.1.5, positive deviations correspond to a less negative value of k_{AB} than the average of k_{AA} and k_{BB}.) Some mixtures, however, have specific A–B interactions, such as solvation or molecular association, that prevent random mixing of the molecules of A and B, and the result is then *negative* deviations from Raoult's law. If the deviations from Raoult's law, either positive or negative, are large enough, the constant-temperature liquidus curve exhibits a maximum or minimum and *azeotropic* behavior results.

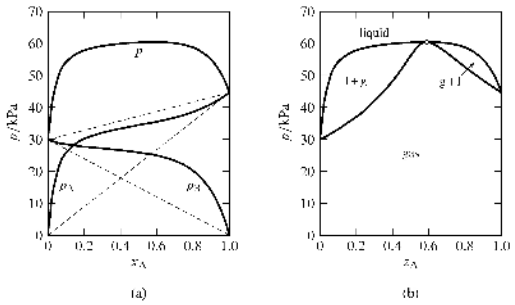


Figure 13.8 Binary system of methanol (A) and benzene at $45\,°C$ (Hossein Toghiani, Rebecca K. Toghiani, and Dabir S. Viswanath, *J. Chem. Eng. Data*, **39**, 63–67, 1994).
(a) Partial pressures and total pressure in the gas phase equilibrated with liquid mixtures. The dashed lines indicate Raoult's law behavior.
(b) Pressure–composition phase diagram at $45\,°C$. Open circle: azeotropic point at $z_A = 0.59$ and $p = 60.5\,kPa$.

Figure 13.8 shows the azeotropic behavior of the binary methanol-benzene system at constant temperature. In Fig. 13.8(a), the experimental partial pressures in a gas phase equilibrated with the nonideal liquid mixture are plotted as a function of the liquid composition. The partial pressures of both components exhibit positive deviations from Raoult's law, consistent with the statement in Sec. 12.8.2 that if one constituent of a binary liquid mixture exhibits positive deviations from Raoult's law, with only one inflection point in the curve of fugacity versus mole fraction, the other constituent also has positive deviations from Raoult's law. The total pressure (equal to the sum of the partial pressures) has a maximum value greater than the vapor pressure of either pure component. The curve of p versus x_A becomes the liquidus curve of the pressure–composition phase diagram shown in Fig. 13.8(b). Points on the vaporus curve are calculated from $p = p_A/y_A$.

> In practice, the data needed to generate the liquidus and vaporus curves of a nonideal binary system are usually obtained by allowing liquid mixtures of various compositions to boil in an equilibrium still at a fixed temperature or pressure. When the liquid and gas phases have become equilibrated, samples of each are withdrawn for analysis. The partial pressures shown in Fig. 13.8(a) were calculated from the experimental gas-phase compositions with the relations $p_A = y_A p$ and $p_B = p - p_A$.

If the constant-temperature liquidus curve has a maximum pressure at a liquid composition not corresponding to one of the pure components, which is the case for the methanol–benzene system, then the liquid and gas phases are mixtures of identical compositions at this pressure. This behavior was deduced at the end of Sec. 12.8.3. On the pressure–composition phase diagram, the liquidus and vaporus curves both have maxima at this pressure, and the two curves coincide at an *azeotropic point*. A binary system with negative deviations from Raoult's law can have an isothermal liquidus curve with a *minimum* pressure at a particular mixture composition, in which case the liquidus and vaporus curves coincide at an azeotropic point at this minimum. The general phenomenon in which equilibrated liquid and gas mixtures have identical compositions is called *azeotropy*, and the liquid with this composition is an azeotropic mixture or **azeotrope** (Greek: *boils unchanged*). An azeotropic mixture vaporizes as if it were a pure substance, undergoing an equilibrium phase transition to a gas of the same composition.

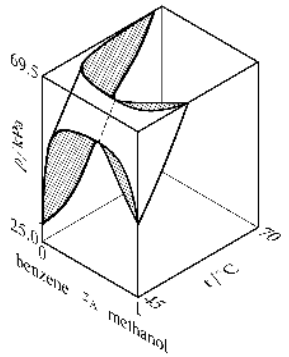


Figure 13.9 Liquidus and vaporus surfaces for the binary system of methanol (A) and benzene (Hossein Toghiani, Rebecca K. Toghiani, and Dabir S. Viswanath, *J. Chem. Eng. Data*, **39**, 63–67, 1994). Cross-sections are hatched in the direction of the tie lines. The dashed curve is the azeotrope vapor-pressure curve.

If the liquidus and vaporus curves exhibit a *maximum* on a pressure–composition phase diagram, then they exhibit a *minimum* on a temperature–composition phase diagram. This relation is explained for the methanol–benzene system by the three-dimensional liquidus and vaporus surfaces drawn in Fig. 13.9. In this diagram, the vaporus surface is hidden behind the liquidus surface. The hatched cross-section at the front of the figure is the same as the pressure–composition diagram of Fig. 13.8(b), and the hatched cross-section at the top of the figure is a temperature–composition phase diagram in which the system exhibits a *minimum-boiling azeotrope*.

A binary system containing an azeotropic mixture in equilibrium with its vapor has two species, two phases, and one relation among intensive variables: $x_A = y_A$. The number of degrees of freedom is then $F = 2 + s - r - P = 2 + 2 - 1 - 2 = 1$; the system is univariant. At a given temperature, the azeotrope can exist at only one pressure and have only one composition. As T changes, so do p and z_A along an *azeotrope vapor-pressure curve* as illustrated by the dashed curve in Fig. 13.9.

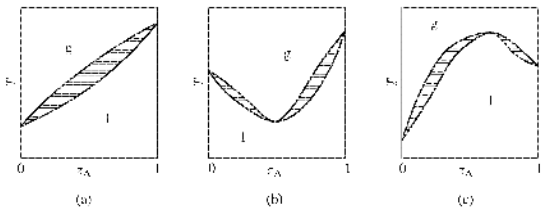


Figure 13.10 Temperature–composition phase diagrams of binary systems exhibiting (a) no azeotropy, (b) a minimum-boiling azeotrope, and (c) a maximum-boiling azeotrope. Only the one-phase areas are labeled; two-phase areas are hatched in the direction of the tie lines.

Figure 13.10 summarizes the general appearance of some relatively simple temperature–composition phase diagrams of binary systems. If the system does not form an azeotrope (*zeotropic* behavior), the equilibrated gas phase is richer in one component than the liquid phase at all liquid compositions, and the liquid mixture can be separated into its two components by fractional distillation. The gas in equilibrium with an azeotropic mixture, however, is not enriched in either component. Fractional distillation of a system with an azeotrope leads to separation into one pure component and the azeotropic mixture.

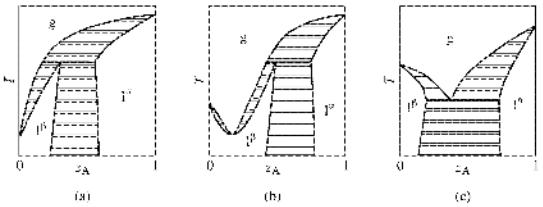


Figure 13.11 Temperature–composition phase diagrams of binary systems with partially-miscible liquids exhibiting (a) the ability to be separated into pure components by fractional distillation, (b) a minimum-boiling azeotrope, and (c) boiling at a lower temperature than the boiling point of either pure component. Only the one-phase areas are labeled; two-phase areas are hatched in the direction of the tie lines.

More complicated behavior is shown in the phase diagrams of Fig. 13.11. These are binary systems with partially-miscible liquids in which the boiling point is reached before an upper consolute temperature can be observed.

Solid–gas systems

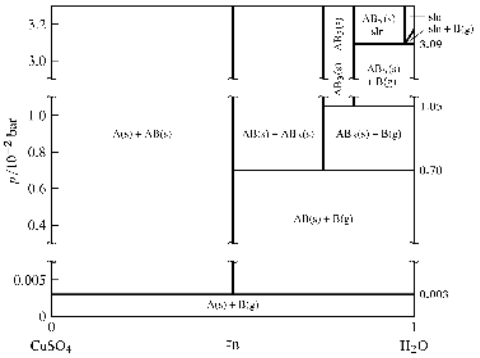


Figure 13.12 Pressure–composition phase diagram for the binary system of $CuSO_4$ (A) and H_2O (B) at **25 °C** (Thomas S. Logan, *J. Chem. Educ.*, **35**, 148–149, 1958; E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. VII, McGraw-Hill, New York, 1930, p. 263).

As an example of a two-component system with equilibrated solid and gas phases, consider the components $\mathbf{CuSO_4}$ and $\mathbf{H_2O}$, denoted A and B respectively. In the pressure–composition phase diagram shown in Fig. 13.12, the composition variable $\boldsymbol{z_B}$ is as usual the mole fraction of component B in the system as a whole.

The anhydrous salt and its hydrates (solid compounds) form the series of solids $\mathbf{CuSO_4}$, $\mathbf{CuSO_4 \cdot H_2O}$, $\mathbf{CuSO_4 \cdot 3\,H_2O}$, and $\mathbf{CuSO_4 \cdot 5\,H_2O}$. In the phase diagram these formulas are abbreviated A, AB, $\mathbf{AB_3}$, and $\mathbf{AB_5}$. The following dissociation equilibria (dehydration equilibria) are possible:

$$\begin{aligned}
\mathbf{CuSO_4 \cdot H_2O(s)} &\rightleftharpoons \mathbf{CuSO_4(s) + H_2O(g)} \\
\tfrac{1}{2}\,\mathbf{CuSO_4 \cdot 3\,H_2O(s)} &\rightleftharpoons \tfrac{1}{2}\,\mathbf{CuSO_4 \cdot H_2O(s) + H_2O(g)} \\
\tfrac{1}{2}\,\mathbf{CuSO_4 \cdot 5\,H_2O(s)} &\rightleftharpoons \tfrac{1}{2}\,\mathbf{CuSO_4 \cdot 3\,H_2O(s) + H_2O(g)}
\end{aligned}$$

The equilibria are written above with coefficients that make the coefficient of $H_2O(g)$ unity. When one of these equilibria is established in the system, there are two components and three phases; the phase rule then tells us the system is univariant and the pressure has only one possible value at a given temperature. This pressure is called the *dissociation pressure* of the higher hydrate.

The dissociation pressures of the three hydrates are indicated by horizontal lines in Fig. 13.12. For instance, the dissociation pressure of $CuSO_4 \cdot 5\,H_2O$ is 1.05×10^{-2} bar. At the pressure of each horizontal line, the equilibrium system can have one, two, or three phases, with compositions given by the intersections of the line with vertical lines. A fourth three-phase equilibrium is shown at $p = 3.09 \times 10^{-2}$ bar; this is the equilibrium between solid $CuSO_4 \cdot 5\,H_2O$, the saturated aqueous solution of this hydrate, and water vapor.

Consider the thermodynamic equilibrium constant of one of the dissociation reactions. At the low pressures shown in the phase diagram, the activities of the solids are practically unity and the fugacity of the water vapor is practically the same as the pressure, so the equilibrium constant is almost exactly equal to p_d/p°, where p_d is the dissociation pressure of the higher hydrate in the reaction. Thus, a hydrate cannot exist in equilibrium with water vapor at a pressure below the dissociation pressure of the hydrate because dissociation would be spontaneous under these conditions. Conversely, the salt formed by the dissociation of a hydrate cannot exist in equilibrium with water vapor at a pressure above the dissociation pressure because hydration would be spontaneous.

> If the system contains dry air as an additional gaseous component and one of the dissociation equilibria is established, the partial pressure p_{H_2O} of H_2O is equal (approximately) to the dissociation pressure p_d of the higher hydrate. The prior statements regarding dissociation and hydration now depend on the value of p_{H_2O}. If a hydrate is placed in air in which p_{H_2O} is less than p_d, dehydration is spontaneous; this phenomenon is called **efflorescence** (Latin: *blossoming*). If p_{H_2O} is greater than the vapor pressure of the saturated solution of the highest hydrate that can form in the system, the anhydrous salt and any of its hydrates will spontaneously absorb water and form the saturated solution; this is **deliquescence** (Latin: *becoming fluid*).

If the two-component equilibrium system contains only two phases, it is bivariant corresponding to one of the areas in Fig. 13.12. Here both the temperature and the pressure can be varied. In the case of areas labeled with two *solid* phases, the pressure has to be applied to the solids by a fluid (other than H_2O) that is not considered part of the system.

Systems at high pressure

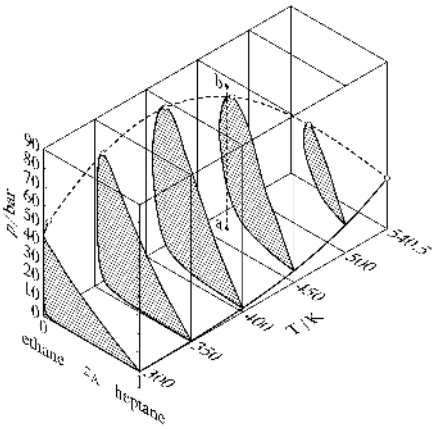


Figure 13.13 Pressure–temperature–composition behavior in the binary heptane–ethane system (W. B. Kay, *Ind. Eng. Chem.*, **30**, 459–465, 1938). The open circles are critical points; the dashed curve is the critical curve. The dashed line a–b illustrates retrograde condensation at 450 K.

Binary phase diagrams begin to look different when the pressure is greater than the critical pressure of either of the pure components. Various types of behavior have been observed in this region. One common type, that found in the binary system of heptane and ethane, is shown in Fig. 13.13. This figure shows sections of a three-dimensional phase diagram at five temperatures. Each section is a pressure–composition phase diagram at constant T. The two-phase areas are hatched in the direction of the tie lines. At the left end of each tie line (at low z_A) is a vaporus curve, and at the right end is a liquidus curve. The vapor pressure curve of pure ethane ($z_A = 0$) ends at the critical point of ethane at $305.4\,K$; between this point and the critical point of heptane at $540.5\,K$, there is a continuous *critical curve*, which is the locus of critical points at which gas and liquid mixtures become identical in composition and density.

Consider what happens when the system point is at point a in Fig. 13.13 and the pressure is then increased by isothermal compression along line a–b. The system point moves from the area for a gas phase into the two-phase gas–liquid area and then out into the gas-phase area again. This curious phenomenon, condensation followed by vaporization, is called *retrograde condensation*.

Under some conditions, an isobaric increase of T can result in vaporization followed by condensation; this is *retrograde vaporization*.

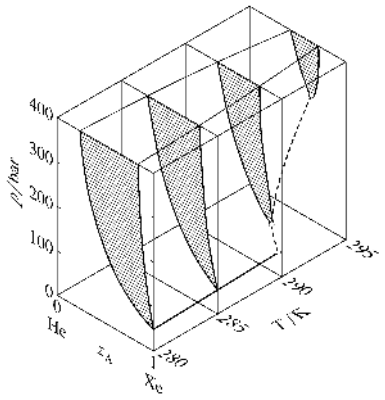


Figure 13.14 Pressure–temperature–composition behavior in the binary xenon–helium system (J. de Swann Arons and G. A. M. Diepen, *J. Chem. Phys.*, **44**, 2322–2330, 1966). The open circles are critical points; the dashed curve is the critical curve.

A different type of high-pressure behavior, that found in the xenon–helium system, is shown in Fig. 13.14. Here, the critical curve begins at the critical point of the less volatile component (xenon) and continues to *higher* temperatures and pressures than the critical temperature and pressure of either pure component. The two-phase region at pressures above this critical curve is sometimes said to represent *gas–gas equilibrium*, or *gas–gas immiscibility*, because we would not usually consider a liquid to exist beyond the critical points of the pure components. Of course, the coexisting phases in this two-phase region are not gases in the ordinary sense of being tenuous fluids, but are instead high-pressure fluids of liquid-like densities. If we want to call both phases gases, then we have to say that pure gaseous substances at high pressure do not necessarily mix spontaneously in all proportions as they do at ordinary pressures.

If the pressure of a system is increased isothermally, eventually solid phases will appear; these are not shown in Figs. 13.13 and Fig. 13.14.

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CHAPTER OVERVIEW

6: Chemical Equilibrium

6.1: Equilibrium Results when Gibbs Energy is Minimized

6.2: An Equilibrium Constant is a Function of Temperature Only

6.3: Gibbs Energy of a Reaction vs. Extent of Reaction is a Minimum at Equilibrium

6.4: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity

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6.1: Equilibrium Results when Gibbs Energy is Minimized

Many important chemical reactions -if not *most*- are performed in *solution* rather than between solids or gases. Solid state reactions are often very slow and not all chemical species can be put in the vapor phase because they decompose before evaporating.

Often we are not concerned with the temporal aspects of a reaction. That can be technologically very important but it is the domain of *kinetics* - a different branch of Physical Chemistry - rather than classical thermodynamics.. The latter is more concerned with the endpoint. This is the thermodynamically speaking the (stable) equilibrium, but chemically it can either represent a *completed* reaction or a *chemical equilibrium*.

Unfortunately, of the three main aggregation states: gas – liquid – solid, the structure of liquids is least understood and one of the most complex liquids is also one of the most extensively used ones: water. It is vital to many branches of chemistry varying from geochemistry to environmental chemistry to biochemistry. We shall make just a small inroad into its complexity.

Extent of reaction

To describe the progress of a reaction we define the **extent of reaction**. It is usually denoted by the Greek letter ξ.

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

Using stoichiometry we can define the extent by considering how the number of moles (or molar amounts) of each species changes during the reaction:

reactants

- $n_A = n_{A,0} - v_A \xi$
- $n_B = n_{B,0} - v_B \xi$

products

- $n_Y = n_{Y,0} + v_Y \xi$
- $n_Z = n_{Z,0} + v_Z \xi$

The dimension of ξ is [mol] because the stoichiometric coefficients v_i are dimensionless integers. If the reaction goes to completion for one of the reactants -the *limiting reactant*- $n_{A \text{ or } B}$=n_{limiting} will go to zero. If we start with $n_{limiting} = v_{limiting}$ moles, the value of ξ starts at 0 (no products) and goes to 1 at completion (limiting reactant depleted). When approaching an equilibrium ξ will not go beyond ξ_{eq}.

Measuring ξ

The extent of reaction is what is the central subject of reaction kinetics. Its value is typically measured as a function of time indirectly by measuring a quantity q that is *linearly dependent* on ξ(t):

$$q(\xi) = a\xi + b$$

Consider the situation at the extremes $\xi = 0$ and $\xi = 1$:

$$q_0 = a.0 + b = b$$

$$q_1 = a.1 + b = a + b$$

$$q_1 - q_0 = a$$

Thus, ξ can be found from

$$\frac{q(t) - q0}{q_1 - q_0} = \frac{q(t) - b}{a}$$

The nature of q can vary widely from UV/Vis absorption, conductivity, gravimetric to caloric data.

In practice, q_0 at $\xi = 0$ is often hard to observe because it takes time to mix the reactants, particularly in solutions, and q_1 at ξ=1 may never be reached if the reaction goes to equilibrium. Nevertheless the values of a and b can often be found from the available data by fitting techniques.

In (equilibrium, static) thermodynamics we are only concerned with the endpoint:

- $\xi = 1$: the reaction runs to completion
- $\xi = \xi_{eq}$: the react ion goes to a state of chemical equilibrium

Thermodynamic Potentials

As we have seen we can write any change in the Gibbs free energy due to changes in the molar amounts of the species involved in the reaction (at T, P constant) as:

$$dG = \sum \frac{\partial G}{\partial n_i} dn_i = \sum \mu_i dn_i$$

where μ is the *thermodynamic potential*, often called *chemical potential* when dealing with reactions. From the definition of ξ we can see by differentiation that

- $dn_A = -v_A d\xi$
- $dn_B = -v_A d\xi$
- $dn_Y = v_Y d\xi$
- $dn_Z = v_Z d\xi$

This allows us to *unify the changes* in the molar amount of all the species into *one single variable* $d\xi$. We get:

$$dG = \left[\sum -v_{i,reactants}\mu_{i,reactants} + \sum +v_{i,products}\mu_{j,products}\right] d\xi$$

or

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\sum v_{i,r}\mu_{i,r} + \sum v_{i,p}\mu_{j,p}$$

This quantity is also written as:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G$$

This quantity gives the change in Gibbs free energy for the reaction (as written!!) for Δξ=1 mole. (Units are [J/mol] therefore). This is the change in Gibbs energy (the slope of G vs ξ) when the extent of reaction changes by one mole with a fixed composition. Equilibrium results when Gibbs energy is at a minimum with respect to the extent of reaction.

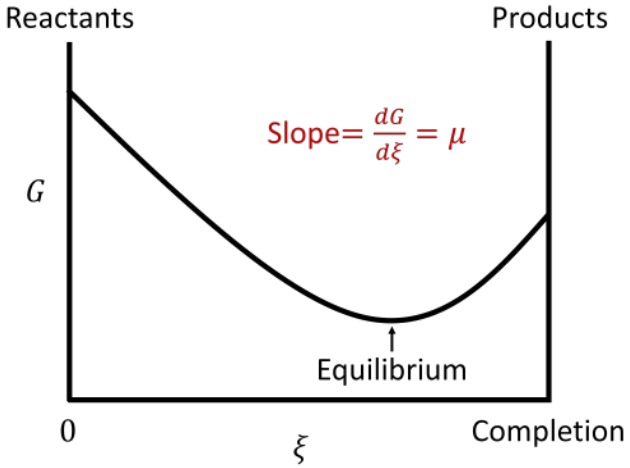


Figure 1. Gibbs energy plotted as a function of the extent of reaction. Equilibrium results when the Gibbs energy is minimized.

Gas Reactions

Let us assume that our reaction is entirely between gas species and that the gas is sufficiently dilute that we can use the ideal gas law. Then we can write for each species:

$$\mu_i = \mu_i^o + RT \ln \frac{P_i}{P_i^o}$$

We can then split up the $\Delta_r G$ expression in two parts:

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

The standard potentials:

$$\Delta_r G^o = -\sum v_{i,r}\, \mu_{i,r}^o + \sum v_{i,p} \mu_{j,p}^o$$

and the logarithmic terms:

$$RT \ln Q = -v_A RT \ln \left(\frac{P_A}{P_A^o} \right) - v_B RT \ln \left(\frac{P_B}{P_B^o} \right) + v_Y RT \ln \left(\frac{P_Y}{P_Y^o} \right) + v_Z RT \ln \left(\frac{P_Z}{P_Z^o} \right)$$

We can combine all the logarithmic terms into Q, called the ***reaction quotient***. The stoichiometric coefficients become exponents and the reactants' factors will be 'upside down' compared to the products, because of the properties of logarithms:

$$a \ln x = \ln x^a$$

$$-a \ln x = \ln \left(\frac{1}{x^a} \right)$$

We have kept the standard pressures P_i^o in the expression, but often they are omitted. They are usually all 1 bar, but in principle we could choose 1 bar for A 1 Torr for B an 1 psi for the products. It creates a valid (though ridiculous) definition of what $^{\ominus}$ stands for. (Of course the value of $\Delta_r G^o$ does *depend* on that choice!).

We could write

$$RT \ln Q = RT \ln \frac{Q_P}{Q^o}$$

Q^o is typically unity in magnitude but it *cancels the dimensions* of Q_P. That means that Q and Q_P are equal in magnitude and we can get Q from Q_P by simply dropping the dimensions. Q is dimensionless but Q_P usually is not. Often this fine distinction is simply not made and Q^o is *omitted*, we get:

$$\Delta_r G = \Delta_r G^o + RT \ln \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}}$$

Notice the difference between $\Delta_r G$ which denotes the conditions (e.g. pressures) of *your reaction* and $\Delta_r G^o$ denotes standard conditions.

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6.2: An Equilibrium Constant is a Function of Temperature Only

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

When the reaction reaches equilibrium, the Gibbs energy of reaction, $\Delta_r G$, goes to zero. In this case, the reaction quotient, Q, is usually rewritten as the **equilibrium constant**, K, and we get:

$$\Delta_r G = \Delta_r G^o + RT \ln K = 0$$

$$\Delta_r G^o = -RT \ln K$$

where

$$K = \frac{P_{eq,Y}^{vY} P_{eq,Z}^{vZ}}{P_{eq,A}^{vA} P_{eq,B}^{vB}}$$

> **Note**
>
> As you see $\Delta_r G^o$ is ***not*** zero, because the standard state does ***not*** represent an equilibrium state (typically).

We can calculate the temperature dependence of K. Rather than look at:

$$\left(\frac{\partial K}{\partial T}\right)_P$$

We will look at:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P$$

Starting with Gibbs energy:

$$\Delta_r G^\circ = -RT \ln K$$

$$\therefore \ln K = -\frac{\Delta r G^\circ}{RT}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{1}{R}\left[\frac{\partial (\Delta_r G^\circ / T)}{\partial T}\right]_P$$

We need to take the Gibbs-Helmholtz equation:

$$\Delta \bar{H} = -T^2 \left[\frac{\partial (\Delta \bar{G}/T)}{\partial T}\right]_P$$

We can also write it as:

$$\left[\frac{\partial \left(\Delta \bar{G}/T\right)}{\partial T}\right]_P = -\frac{\Delta \bar{H}}{T^2}$$

Plugging the Gibbs-Helmholtz equation into our earlier equation, we obtain the Van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2}$$

The temperature dependence of the equilibrium constant depends on enthalpy of reaction. Rearranging:

$$d(\ln K) = \frac{\Delta_r H^\circ (T)}{RT^2} dT$$

This is the Van't Hoff equation. We can use it to find K at other temperatures. Assuming enthalpy is independent of temperature, the integrated form becomes:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Le Chatelier's Principle

In the ideal gas reaction case, K **only** depends on temperature, T, (just like U) not on the total pressure, P. This leads to the well-known principle of Le Chatelier. Consider a gas reaction like:

\[A \rightleftharpoons B + C \nonumber \nonumber \]

e.g.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

In pressures, the equilibrium constant becomes:

$$K = \frac{P_B P_C}{P_A}$$

If initially n_A =1 we have at an extent ξ:

n_A = 1- ξ

n_B= ξ

n_C= ξ

n_{Total} = 1+ ξ

The partial pressures are given by Dalton's law:

P_A= [1- ξ /1+ ξ] P

P_B [ξ / 1+ ξ] P

P_C [ξ /1+ ξ] P

The equilibrium constant becomes:

$$K = P\frac{\xi_{eq}^2}{1-\xi_{eq}^2}$$

Even though the total pressure, P, does occur in this equation, K is *not* dependent on P. If the total pressure is changed (e.g. by compression of the gas) the value of ξ_{eq} will change (the equilibrium shifts) in response. It will go to the side with the fewer molecules. This fact is known as le Chatelier's principle

If the system is not ideal we will also get a Chatelier shift, but the value of K may change a little because the value of the activity coefficients (or fugacity) is a little dependent on the pressure too. In solution the same thing holds. In ideal solutions K is only T dependent, but as we saw these systems are rare. Particularly in ionic solutions equilibrium constants will be effected by other things than just temperature, e.g. changes in the ionic strength and we need to find the activity coefficients to make any predictions.

Example

Consider the reaction of ammonia decomposition:

$$2NH_3\,(g) \leftrightharpoons N_2\,(g) + 3H_2\,(g)$$

$$\Delta_f H^\circ(NH_3, g) = -45.90\ \text{kJ/mol}$$

The reaction is initially at equilibrium. For each of the stresses, use your General Chemistry knowledge to decide if equilibrium will be unaffected, or if it will shift towards reactants or products.

Process	Shifts towards
Isothermal removal of H_2 gas	
Isothermal addition of N_2 gas	
Isothermal decrease of container volume	
Isothermal and isochoric addition of argon gas	
Isobaric increase of temperature	

Write the equilibrium constant expression for the above chemical reaction in terms of gas-phase mole fractions.

Concentration

The gas law contains a hidden definition of concentration:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = cRT$$

$$c = \frac{P}{RT} \tag{6.2.1}$$

Here c stands for the molar amount per unit volume or ***molarity***. For gaseous mixtures we do not use this fact much, but it provides the link to the more important liquid solution as a reaction medium. We can rewrite the equilibrium constant as

$$K = \frac{c_{eq,Y}^{v_Y} c_{eq,Z}^{v_Z}}{c_{eq,A}^{v_A} c_{eq,B}^{v_B}} \tag{6.2.2}$$

However, c (Equation 6.2.1) is substituted into K (Equation 6.2.2), then not all the factors of RT cancel. The missing term g. ln[RT] depends on the stoichiometric coefficients:

$$g = v_Y + v_Z - v_A - v_B$$

The term is generally *incorporated* in $\Delta_r G^\circ$ so that the latter now refers to a new standard state of 1 mole per liter of each species rather than 1 bar of each (or so).

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6.3: Gibbs Energy of a Reaction vs. Extent of Reaction is a Minimum at Equilibrium

As discussed in Section 26.4, we defined the extent of the reaction (ξ) as a quantitative measure of how far along the reaction has evolved. For simple reactions like $\mathbf{A} \rightleftharpoons \mathbf{B}$, the extent of reaction is easy to define and is simply the number of moles of **A** that has been converted to **B**. Since $d\xi$ has the same value as dn, we can write that

$$\begin{aligned} dG &= \mu_A dn_A + \mu_B dn_B \\ &= -\mu_A d\xi + \mu_B d\xi. \end{aligned}$$

The minus sign comes from the fact that when the reaction goes in the left to right direction, the amount of **A** is decreasing, while the amount of **B** is increasing. Looking at these equations, it is reasonable to suggest that:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = \mu_B - \mu_A$$

This is the slope of the free energy with respect to the extent of the reaction. This relationship will have a region where the sign is negative, one point where the value is zero and a region where the value is positive (Figure **6.3.1**). If we look at a plot of G as a function of ξ, we can see that the point where is the minimum of the curve:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = 0$$

This is the point where μ_A and μ_B are the same. On one side of the minimum, the slope is negative and on the other side, the slope is positive. In both cases, the reaction is spontaneous (i.e, $dG < 0$) as long as the reaction is evolving towards the minimum, which will be called the **equilibrium position**. Hence, all reactions spontaneously move towards equilibrium; the immediate question is what value of ξ corresponds to the equilibrium position of a reaction?

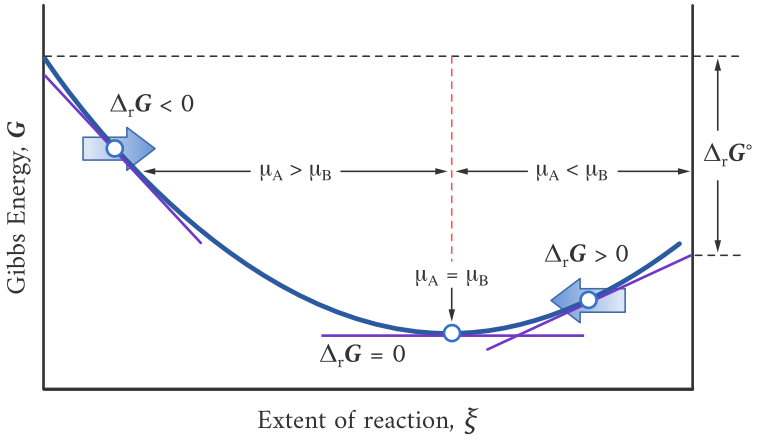


Figure **6.3.1**: Reactive Gibbs Energy and Equilibria. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Terminology

- A reaction for which $\Delta_r G < 0$ is called **exergonic**.
- A reaction for which $\Delta_r G > 0$ is called **endergonic**.
- $\Delta_r G < 0$, the forward reaction is spontaneous.
- $\Delta_r G > 0$, the reverse reaction is spontaneous.
- $\Delta_r G = 0$, the reaction is at equilibrium.

Ideal Gas Equilibrium

To understand how we can find the minimum and what the Gibbs free energy of a reaction depends on, let's first start with a reaction that converts one ideal gas into another.

$$\mathbf{A} \rightleftharpoons \mathbf{B}$$

Let's assume the reaction enthalpy is zero and hence the only thing that determines what the ratio of product to reactant should be is the entropy term (the mixing term), which is the most favorable when the mixture is half and half.

$$\Delta G_{\text{mix}} = nRT\left(\chi_A \ln \chi_A + \chi_B \ln \chi_B\right) \tag{6.3.1}$$

Remember that the Gibbs free energy of mixing is not a molar quantity and depends on n (unlike the reaction Gibbs free energy). Also, the Gibbs free energy of mixing is defined relative to pure **A** and **B**. The free energy of mixing in Equation 6.3.1 is at a minimum when the amounts of **A** equal **B**.

Thus, if we have a reaction $\mathbf{A} \rightleftharpoons \mathbf{B}$ and there is no enthalpy term (and no change in the inherent entropy of A vs. B), we would expect the system to have the minimum Gibbs free energy when the mole fraction of **A** and **B** are each 0.5.

Think about it

If **A** can form **B** and **B** can form **A** and there is no other forces involved (no heat/enthalpy) that would favor one product over the other, probability would just state that eventually you will have statistically the same amount of both A and B present -- this is the lowest free energy state. (This, of course, will not be true if the enthalpy for the reaction is not zero or if **A** and **B** have different inherent entropies). Usually there are additional terms for the reaction.

Lets work through this for an ideal gas reaction:

$$\begin{aligned}\Delta_r G &= \mu_B - \mu_A \\ &= \mu_B^o + RT\ln\frac{P_B}{P^\theta} - \mu_A^o - RT\ln\frac{P_A}{P^\theta} \\ &= \mu_B^o - \mu_A^o + RT\ln\frac{P_B}{P_A}\end{aligned}$$

What we normally do at this point is to give the first two terms a special name. Since it is the difference between the chemical potentials at standard conditions, we refer to it as the Gibbs free energy of reaction at standard conditions or the **standard Gibbs free energy of reaction**.

$$\begin{aligned}\Delta_r G^o &= \mu_B^o - \mu_A^o \\ \Delta_r G &= \Delta_r G^o + RT\ln\frac{P_B}{P_A}\end{aligned} \tag{6.3.2}$$

There are two parts to Equation 6.3.2. The first term ($\Delta_r G^o$) is the Gibbs free energy for converting one mole of **A** to **B** under standard conditions (1 bar of both **A** and **B**). The second term is the mixing term that is minimized when the amounts of A and B are equal to one another (Figure 6.3.2). The first term you look up in a reference book and is specific for a specific reaction. The second term is calculated knowing the partial pressures of **A** and **B** in the gas.

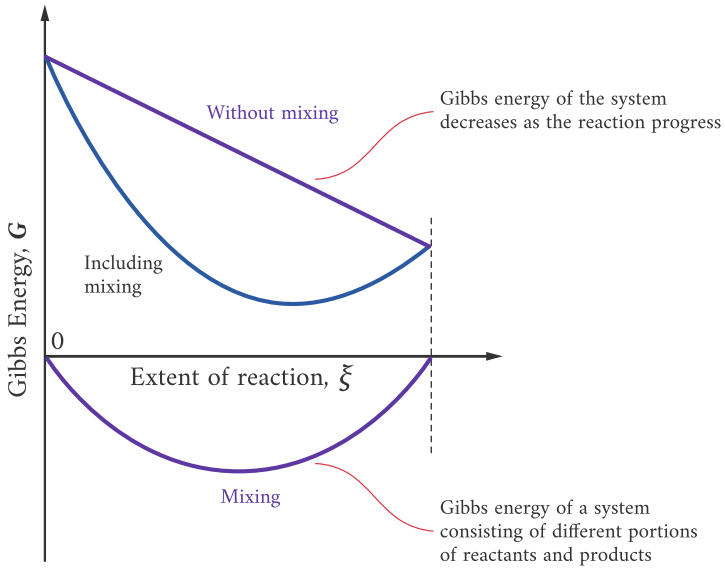


Figure **6.3.2**: Molecular interpretation of the minimum in the reaction Gibbs energy Gibbs energy of the system decreases as the reaction progress Gibbs energy of a system consisting of different portions of reactants and products. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Now the minimum absolute Gibbs free energy will occur at the bottom of the curve where the slope is zero. Thus, the lowest free energy will occur when the reaction free energy (i.e., the slope of that curve in Figure **6.3.1**) is equal to zero. The chemical potentials of **A** and **B** are equal.

$$\mu_A = \mu_B$$

At this point, the reaction will neither go forwards or backwards and we call this equilibrium. Hence, at equilibrium:

$$\begin{aligned}\Delta_r G &= \Delta_r G^o + RT \ln \frac{P_B}{P_A} \\ &= 0\end{aligned}$$

and the specific ratio of P_A and P_B necessary to ensure $\Delta_r G = 0$ is characteristic of the reaction and is called the **equilibrium constant** for that reaction.

$$K_{eq} = \frac{P_B}{P_A}$$

We can now relate thermodynamic quantities to concentrations of molecules at equilibrium. We can also see that at equilibrium:

$$\begin{aligned}0 &= \Delta_r G^o + RT \ln K_{eq} \\ \Delta_r G^o &= -RT \ln K_{eq} \\ K_{eq} &= e^{-\frac{\Delta_r G^o}{RT}}\end{aligned}$$

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6.4: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity

It is important to distinguish between the Gibbs energy of reaction, $\Delta_r G$ and the standard state Gibbs energy of reaction, $\Delta_r G°$. The ° refers to standard state conditions. That is, each reactant and product has a partial pressure of 1 bar if a gas, a concentration of 1 M if a solution, and they are all unmixed from each other. Such idealized conditions, while convenient for serving as a reference state, do not actually represent real reaction conditions. Consider the reaction of nitrogen with hydrogen to form ammonia:

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g)$$

$$\Delta_r G° = -32.9\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

If the reaction was run under standard state conditions (1 bar partial pressure of each gas), the reaction would shift towards the products since $\Delta_r G° < 0$. That is, the partial pressures of N_2 and O_2 will decrease and the partial pressure of NH_3 will increase until equilibrium is reached. The Gibbs energy of reaction is dependent on the composition:

$$\Delta_r G = \Delta_r G° + RT \ln Q = \Delta_r G° + RT \ln \left(\frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}} P_{\mathrm{H_2}}^3} \right)$$

At equilibrium, the minimum Gibbs energy of reaction will be reached:

$$\Delta_r G = 0\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

And the reaction quotient will equal the equilibrium constant:

$$Q = K$$

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6.5: The van 't Hoff Equation

We can use Gibbs-Helmholtz to get the temperature dependence of K

$$\left(\frac{\partial[\Delta G^o/T]}{\partial T}\right)_P = \frac{-\Delta H^o}{T^2}$$

At equilibrium, we can equate ΔG^o to $-RT\ln K$ so we get:

$$\left(\frac{\partial[\ln K]}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2}$$

We see that whether K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative. If temperature is changed little enough that ΔH^o can be considered constant, we can translate a K value at one temperature into another by integrating the above expression, we get a similar derivation as with melting point depression:

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

If more precision is required we could correct for the temperature changes of ΔH^o by using heat capacity data.

> *How K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative.*

The expression for K is a rather sensitive function of temperature given its exponential dependence on the difference of stoichiometric coefficients One way to see the sensitive temperature dependence of equilibrium constants is to recall that

$$K = e^{-\Delta_r G^o/RT} \tag{6.5.1}$$

However, since under constant pressure and temperature

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Equation 6.5.1 becomes

$$K = e^{-\Delta H^o/RT} e^{\Delta S^o/R} \tag{6.5.2}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \tag{6.5.3}$$

which is known as the van 't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.

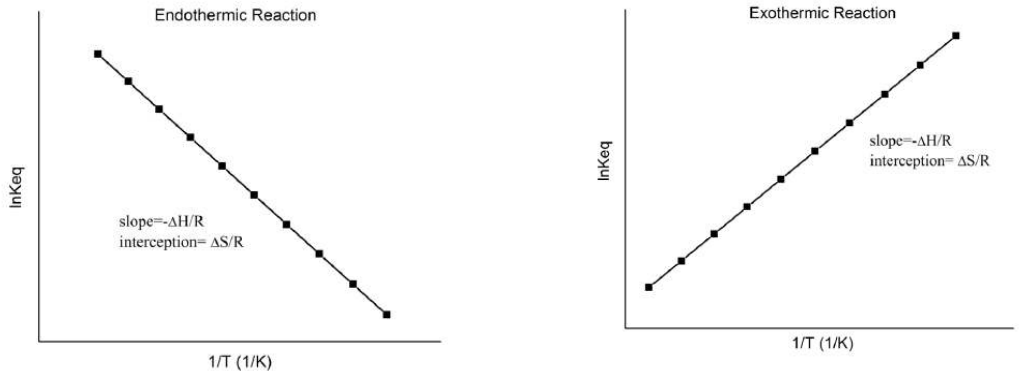


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

Hence, these quantities can be determined from the $\ln K$ vs. $1/T$ data without doing calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on T, which is usually valid.

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CHAPTER OVERVIEW

7: Kinetics

Physical Chemistry: Thermodynamics
Patrick Fleming

Chemical kinetics is the study of how fast chemical reactions proceed from reactants to products. This is an important topic because while thermodynamics will tell us about the direction of spontaneous change, it is silent as to how fast processes will occur. But additionally, the power of studying reaction rates is that it gives us insight into the actual pathways chemical processes follow to proceed from reactants to products.

7.1: Reaction Rate
7.2: Rate Laws
7.3: 0th order Rate Law
7.4: 1st order rate law
7.5: 2nd order Rate Laws
7.6: The Method of Initial Rates
7.7: Temperature Dependence
7.8: Collision Theory
7.9: Transition State Theory
7.10: Reaction Mechanisms
7.11: The Connection between Reaction Mechanisms and Reaction Rate Laws
7.12: The Rate Determining Step Approximation
7.13: The Steady-State Approximation
7.14: The Equilibrium Approximation

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7.1: Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 7.1.1:

Under a certain set of conditions, the rate of the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\ M/s$$

$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\ M/s$$

$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\ M/s$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

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7.2: Rate Laws

A rate law is any mathematical relationship that relates the concentration of a reactant or product in a chemical reaction to time. Rate laws can be expressed in either derivative (or ratio, for finite time intervals) or integrated form. One of the more common general forms a rate law for the reaction

$$A + B \rightarrow products$$

may take is

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}$$

where k, α, and β are experimentally determined values. However, a rate law can take many different forms, some of which can be quite intricate and complex. The powers α and β need not be integers. For example

$$\text{rate} = k[A]^{\alpha}[B]^{1/2} \tag{7.2.1}$$

is a rate law that is observed for some reactions. Sometimes, the concentrations of products must be included.

$$\text{rate} = \frac{k[A]^{1/2}[B]}{[P]}$$

In some cases, the concentration for a catalyst or enzyme is important. For example, many enzyme mitigated reactions in biological systems follow the Michaelis-Menten rate law, which is of the form

$$\text{rate} = \frac{V_{max}[S]}{K_m + [S]}$$

where V_{max} and K_M are factors that are determined experimentally, and $[S]$ is the concentration of the substrate in the reaction.

Order

For those cases where the rate law can be expressed in the form

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$$

where A, B, and C are reactants (or products or catalysts, etc.) involved in the reaction, the reaction is said to be of α order in A, β order in B, and γ order in C. The reaction is said to be $\alpha + \beta + \gamma$ order overall. Some examples are shown in the following table:

Table 11.3.1: Example Rate Laws

Rate law	Order with respect to A	Order with respect to B	Order with respect to C	Overall order
$\text{rate} = k$	0	0	0	0
$\text{rate} = k[A]$	0	0	0	1
$\text{rate} = k[A]^2$	0	0	0	2
$\text{rate} = k[A][B]$	0	1	0	2
$\text{rate} = k[A]^2[B]$	0	1	0	3
$\text{rate} = k[A][B][C]$	0	1	1	3

Reaction orders can also be fractional such as for Equation 7.2.1 which is 1st order in A, and half order in B. The order can also be negative such as

$$\text{rate} = k\frac{[A]}{[B]}$$

which is 1st order in A, and -1 order in B. In this case, an build-up of the concentration of B will retard (slow) the reaction.

In all cases, the order of the reaction with respect to a specific reactant or product (or catalyst, or whatever) must be determined experimentally. As a general rule, the stoichiometry cannot be used to predict the form of the rate law. However, the rate law can be used to gain some insight into the possible pathways by which the reaction can proceed. That is the topic of Chapter 12. For now we will focus on three useful methods that are commonly used in chemistry to determine the rate law for a reaction from experimental data.

Empirical Methods

Perhaps the simplest of the methods to be used are the empirical methods, which rely on the qualitative interpretation of a graphical representation of the concentration vs time profile. In these methods, some function of concentration is plotted as a function of time, and the result is examined for a linear relationship. For the following examples, consider a reaction of the form

$$A + B \rightarrow products$$

in which A is one of the reactants. In order to employ these empirical methods, one must generate the forms of the integrated rate laws.

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7.3: 0th order Rate Law

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt} = k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A] = -k \int_{t_o}^{t} dt$$

which yields

$$[A] - [A]_o = -kt$$

or

$$[A] = [A]_o - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0^{th} order kinetics. If they are not, other possibilities must be considered.

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7.4: 1st order rate law

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \tag{7.4.1}$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is $\ln[A]_0$.

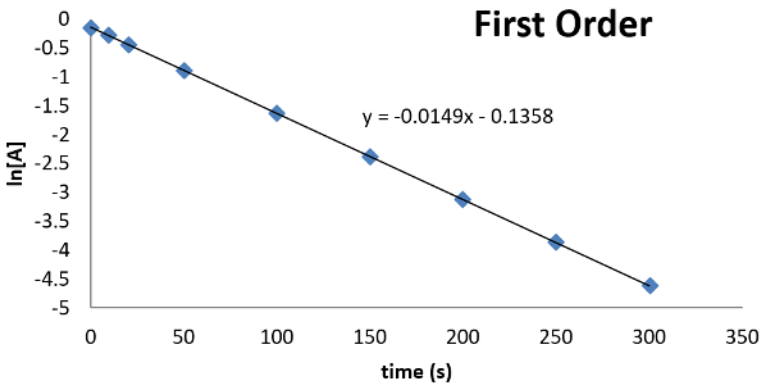
Example 7.4.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation 7.4.1) can be expressed in exponential form:

$$[A] = [A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

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7.5: 2nd order Rate Laws

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{7.5.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{7.5.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 7.5.2 is

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2nd order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A + B \rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt} = k[A][B]$$

and

$$-\frac{d[B]}{dt} = k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A] = [A]_o - [P] \tag{7.5.3}$$

and

$$[B] = [B]_o - [P] \tag{7.5.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt} = k[A][B] \tag{7.5.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 7.5.3 and 7.5.4) into the rate law expression (Equation 7.5.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{7.5.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o - [P])([B] = [B]_o - [P])} = k\,dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]} \frac{d[P]}{([A]_o - [P])([B]_o - [P])} = \int_{t=0}^{t} k\,dt$$

Consulting a table of integrals reveals that for $a \neq b$[1],

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0 \neq [B]_0$) results in

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right)\Bigg|_0^{[A]} = kt\Big|_0^t$$

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right) - \frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right) = kt \tag{7.5.7}$$

Substituting Equations 7.5.3 and 7.5.4 into Equation 7.5.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right) = kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m = ([B]_0 - [A]_0)k.$$

In the limit at $[A]_0 = [B]_0$, then $[A] = [B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate} = k[A]^2$$

and integrate direct like in Equation 7.5.1 and the integrated rate law is (as before)

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

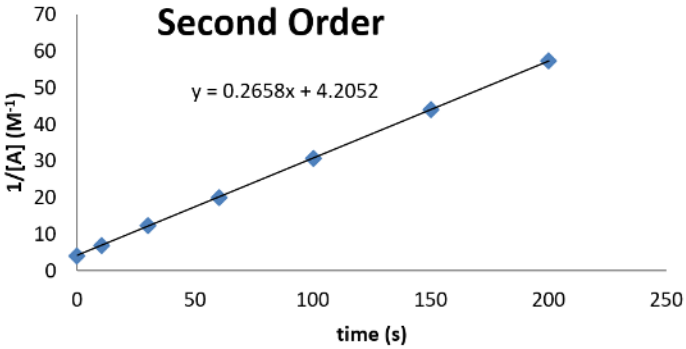
Example 7.5.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

---

[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

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7.6: The Method of Initial Rates

The **method of initial rates** is a commonly used technique for deriving rate laws. As the name implies, the method involves measuring the initial rate of a reaction. The measurement is repeated for several sets of initial concentration conditions to see how the reaction rate varies. This might be accomplished by determining the time needed to exhaust a particular amount of a reactant (preferably one on which the reaction rate does not depend!) A typical set of data for a reaction

$$A + B \rightarrow products$$

might appear as follows:

Run	[A] (M)	[B] (M)	Rate (M/s)
1	0.0100	0.0100	0.0347
2	0.0200	0.0100	0.0694
3	0.0200	0.0200	0.2776

The analysis of this data involves taking the ratios of rates measured where one of the concentrations does not change. For example, assuming a rate law of the form

$$\text{rate} = k[A]^{\alpha}[B]^{\beta} \tag{7.6.1}$$

The ratio of runs i and j generate the following relationship.

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[A]_i^{\alpha}[B]_i^{\beta}}{k[A]_j^{\alpha}[B]_j^{\beta}}$$

So using runs **1** and **2**,

$$\frac{0.0347\,M/s}{0.0694\,M/s} = \frac{\cancel{k}\,(0.01\,M/s)^{\alpha}\,\cancel{(0.01\,M/s)^{\beta}}}{\cancel{k}\,(0.02\,M/s)^{\alpha}\,\cancel{(0.01\,M/s)^{\beta}}}$$

this simplifies to

$$\frac{1}{2} = \left(\frac{1}{2}\right)^{\alpha}$$

So clearly, \(\alpha = 1\) and the reaction is 1st order in A. Taking the ratio using runs 2 and 3 yields

$$\frac{0.0694\,M/s}{0.2776\,M/s} = \frac{\cancel{k}\,(0.02\,M)^{\alpha}\,\cancel{(0.01\,M)^{\beta}}}{\cancel{k}\,(0.02\,M)^{\alpha}\,\cancel{(0.02\,M)^{\beta}}}$$

This simplifies to

$$\frac{1}{4} = \left(\frac{1}{2}\right)^{\beta} \tag{7.6.2}$$

By inspection, one can conclude that \(\beta = 2\), and that the reaction is second order in B. But if it is not so clear (as it might not be if the concentration is not incremented by a factor of 2), the value of \(\beta\) can be determined by taking the natural logarithm of both sides of the Equation 7.6.2.

$$\ln\frac{1}{4} = \ln\left(\frac{1}{2}\right)^{\beta}$$

$$= \beta \ln\left(\frac{1}{2}\right)$$

dividing both sides by $\ln(1/2)$

$$\frac{\ln\left(\frac{1}{4}\right)}{\ln\left(\frac{1}{2}\right)} = \beta\frac{\ln\left(\frac{1}{2}\right)}{\ln\left(\frac{1}{2}\right)}$$

or

$$\beta = \frac{-1.3863}{-0.69315} = 2$$

And so the rate law (Equation 7.6.1) can be expressed as

$$\text{rate} = k[A][B]^2$$

And is 1st order in A, 2nd order in B, and 3rd order overall. The rate constant can then be evaluated by substituting one of the runs into the rate law (or using all of the data and taking an average). Arbitrarily selecting the first run for this,

$$0.0347\,M/s = k(0.01\,M/s)(0.01\,M/s)^2$$

This results in a value of k

$$k = \frac{0.0347\,M/s}{(0.01\,M/s)(0.01\,M/s)^2} = 3.47 \times 10^5\,M^{-2}s^{-1}$$

It is useful to note that the units on k are consistent with a 3rd order rate law.

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7.7: Temperature Dependence

In general, increases in temperature increase the rates of chemical reactions. It is easy to see why, since most chemical reactions depend on molecular collisions. And as we discussed in Chapter 2, the frequency with which molecules collide increases with increased temperature. But also, the kinetic energy of the molecules increases, which should increase the probability that a collision event will lead to a reaction. An empirical model was proposed by Arrhenius to account for this phenomenon. The **Arrhenius model** (Arrhenius, 1889) can be expressed as

$$k = Ae^{-E_a/RT}$$

Although the model is empirical, some of the parameters can be interpreted in terms of the energy profile of the reaction. E_a, for example, is the **activation energy**, which represents the energy barrier that must be overcome in a collision to lead to a reaction.

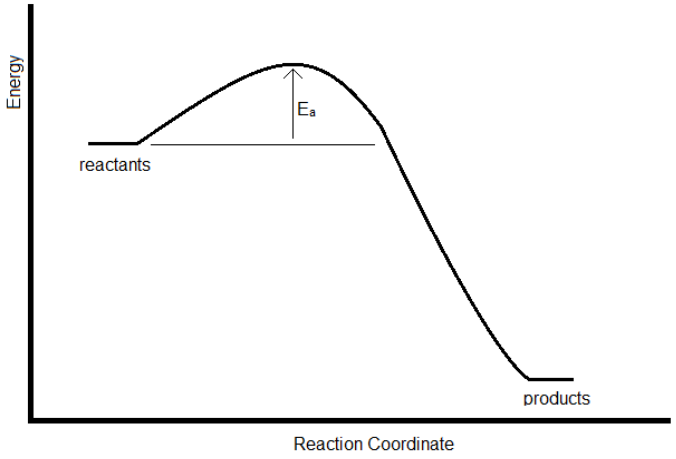


Figure 11.9.1: Reaction profile for an elementary sttep over an activated barrier of height E_a.

If the rate constant for a reaction is measure at two temperatures, the activation energy can be determined by taking the ratio. This leads to the following expression for the Arrhenius model:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7.7.1}$$

Example 7.7.1:

For a given reaction, the rate constant doubles when the temperature is increased form 25 °C to 35 °C. What is the Arrhenius activation energy for this reaction?

Solution

The energy of activation can be calculated from the Arrhenius Equation (Equation 7.7.1).

$$\ln\left(\frac{2k_1}{k_1}\right) = -\frac{E_a}{8.314\,\frac{J}{mol\,K}}\left(\frac{1}{308\,K} - \frac{1}{298\,K}\right)$$

From this reaction:

$$E_a = 52.9\,kJ/mol$$

Preferably, however, the rate constant is measured at several temperatures, and then the activation energy can be determined using all of the measurements, by fitting them to the expression

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

This can be done graphically by plotting the natural logarithm of the rate constant as a function of $1/T$ (with the temperature measured in K). The result should be a straight line (for a well-behaved reaction!) with a slope of $-E_a/R$.

There are some theoretical models (such as collision theory and transition state theory) which suggest the form of the Arrhenius model, but the model itself is purely empirical. A general feature, however, of the theoretical approaches is to interpret the activation energy as an energy barrier which a reaction must overcome in order to lead to a chemical reaction.

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7.8: Collision Theory

Collision Theory was first introduced in the 1910s by Max Trautz (Trautz, 1916) and William Lewis (Lewis, 1918) to try to account for the magnitudes of rate constants in terms of the frequency of molecular collisions, the collisional energy, and the relative orientations of the molecules involved in the collision.

The rate of a reaction, according to collision theory, can be expressed as

$$\text{rate} = Z_{ab}F \tag{7.8.1}$$

where Z_{AB} is the frequency of collisions between the molecules A and B involved in the reaction, and F is the fraction of those collisions that will lead to a reaction. The factor F has **two** important contributors, the energy of the collision and the orientation of the molecules when they collide. The first term, Z_{AB}, can be taken from the kinetic molecular theory discussed in Chapter 2.

$$Z_{AB} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}[A][B] \tag{7.8.2}$$

Where the first term is the average relative velocity in which μ is the reduced mass of the A-B collisional system, σ_{AB} is the collisional cross section, and $[A]$ and $[B]$ are the concentrations of A and B.

The factor F depends on the activation energy. Assuming a Boltzmann (or Boltzmann-like) distribution of energies, the fraction of molecular collisions that will have enough energy to overcome the activation barrier is given by

$$F = e^{-E_a/RT} \tag{7.8.3}$$

Combining Equations 7.8.2 and 7.8.3, the rate of the reaction (Equation 7.8.1) is predicted by

$$\text{rate} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}e^{-E_a/RT}[A][B]$$

So if the rate law can be expressed as a second order rate law

$$\text{rate} = k[A][B]$$

it is clear that the rate constant k is given by

$$k = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}e^{-E_a/RT}$$

By comparison, the theory predicts the form of the **Arrhenius prefactor** to be

$$A = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}$$

It should be noted that collision theory appears to apply only to **bimolecular reactions**, since it takes two molecules to collide. But there are many reactions that have first order rate laws, but are initiated by bimolecular steps in the mechanisms. (Reaction mechanisms will form a large part of the discussion in Chapter 12.) Consider as an example, the decomposition of N_2O_5, which follows the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

Under a certain set of conditions, the following concentrations are observed as a function of time.

time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
0	0.0260	0.0000	0.0000
100	0.0219	0.0081	0.0016
200	0.0185	0.0150	0.0030
300	0.0156	0.0207	0.0041
400	0.0132	0.0256	0.0051
500	0.0111	0.0297	0.0059
600	0.0094	0.0332	0.0066
700	0.0079	0.0361	0.0072

Graphically, these data look as follows:

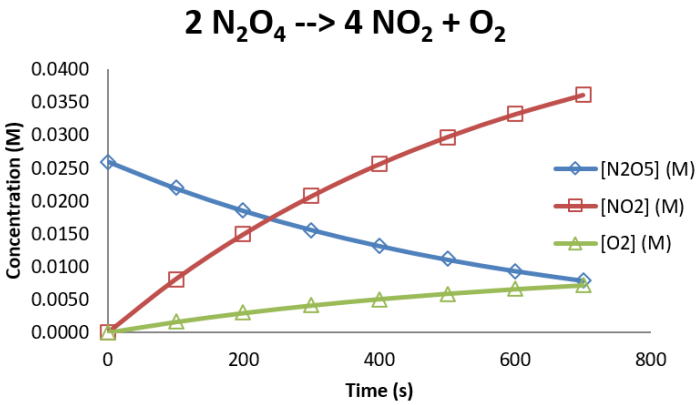
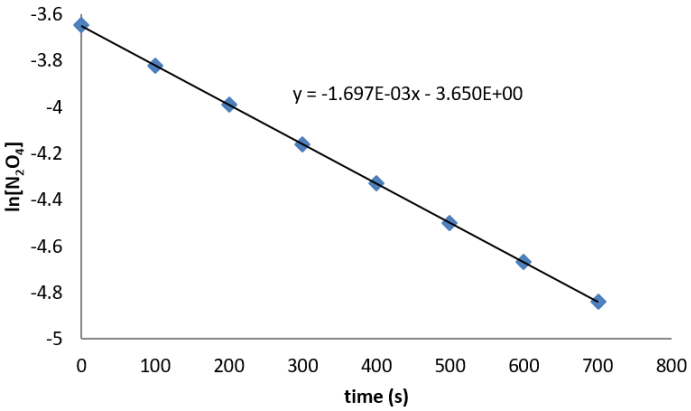


Figure 10.11.1: Concentration kinetics of the thermal decomposition reaction of N_2O_5.

The data for N_2O_5 can be analyzed empirically to show that the reaction is first order in N_2O_5, with a rate constant of 1.697 x 10^{-3} s^{-1}. (The graph is shown below.) So the rate law for the reaction is

$$\text{rate} = 1.697 \times 10^{-3} s^{-1} [N_2O_5]$$

So how can collision theory be used to understand the rate constant? As it turns out, the mechanism for the reaction involves a bimolecular initiation step.



The mechanism for the reaction has a bimolecular initiation step

$$N_2O_5 + M \rightleftharpoons N_2O_5^* + M$$

where $N_2O_5^*$ is an energetically activated form of N_2O_5 which can either relax to reform N_2O_5 or decompose to form the products of the reaction. Because the initiation step is bimolecular, collision theory *can* be used to understand the rate law, but because the product of the unimolecular step undergoes slow conversion to products unimolecularly, the overall rate is observed to be first order in N_2O_5. The analysis of reaction mechanisms, and reconciliation with observed rate laws, form the subjects of Chapter 12.

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7.9: Transition State Theory

Transition state theory was proposed in 1935 by Henry Erying, and further developed by Merrideth G. Evans and Michael Polanyi (Laidler & King, 1983), as another means of accounting for chemical reaction rates. It is based on the idea that a molecular collision that leads to reaction must pass through an intermediate state known as the transition state. For example, the reaction

$$A + BC \rightarrow AB + C$$

would have an intermediate (ABC) where the $B-C$ bond is partially broken, and the $A-B$ bond is partially formed.

$$A + B - C \rightarrow (A - B - C)^{\ddagger} \rightarrow A - B + C$$

So the reaction is mediated by the formation of an activated complex (denoted with the double-dagger symbol ‡) and the decomposition of that complex into the reaction products. Using this theory, the rate of reaction can be expressed as the product of two factors

$$\textbf{rate} = (\textbf{transition state concentration}) \times (\textbf{decomposition frequency})$$

If the formation of the activated complex is considered to reach an equilibrium,

$$K^{\ddagger} = \frac{[ABC]^{\ddagger}}{[A][BC]}$$

So the concentration of the transition state complex can be expressed by

$$[ABC]^{\ddagger} = K^{\ddagger}[A][BC]$$

Using the relationship from Chapter 9 for the equilibrium constant, $K^{\ddagger}$ can be expressed in terms of the free energy of formation of the complex (\(\Delta G^‡\))

$$K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$$

And so the reaction rate is given by

$$\textbf{rate} = (\textbf{frequency})[A][BC]e^{-\Delta G^{\ddagger}/RT}$$

and the remaining task is to derive an expression for the frequency factor. If the frequency is taken to be equal to the vibrational frequency for the vibration of the bond being broken in the activated complex in order to form the reaction products, it can be expressed in terms of the energy of the oscillation of the bond as the complex vibrates.

$$E = h\nu = k_B T$$

or

$$\nu = \frac{k_B T}{h}$$

The reaction rate is then predicted to be

$$\textbf{rate} = \frac{k_B T}{h}[A][BC]e^{-\Delta G^{\ddagger}/RT}$$

And the rate constant is thus given by

$$k = \frac{k_B T}{h}e^{-\Delta G^{\ddagger}/RT}$$

An alternative description gives the transition state formation equilibrium constant in terms of the partition functions describing the reactants and the transition state:

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}}e^{-\Delta G^{\ddagger}/RT}$$

where Q_i is the **partition function** describing the i^{th} species. If the partition function of the transition state is expressed as a product of the partition function excluding and contribution from the vibration leading to the bond cleavage that forms the products and the partition function of that specific vibrational mode

$$Q^{\ddagger} = Q^{\ddagger'} q_v^{\ddagger}$$

In this case, $q_v^{\ddagger}$ can be expressed by

$$q_v^{\ddagger} = \frac{1}{1 - e^{-h\nu^{\ddagger}/RT}} \approx \frac{k_B T}{h\nu^{\ddagger}}$$

So the equilibrium constant can be expressed

$$K^{\ddagger} = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}} e^{-\Delta G^{\ddagger}/RT}$$

And so the rate constant, which is the product of $n^{\ddagger}$ and $K^{\ddagger}$, is given by

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}} e^{-\Delta G^{\ddagger}/RT}$$

which looks very much like the Arrhenius equation proposed quite a few years earlier! Thus, if one understands the vibrational dynamics of the activated complex, and can calculate the partition functions describing the reactants and the transition state, one can, at least in theory, predict the rate constant for the reaction. In the next chapter, we will take a look at how kinetics studies can shed some light on chemical reaction mechanisms.

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7.10: Reaction Mechanisms

A **reaction mechanism** is a set of **elementary reactions** steps, that when taken in aggregate define a chemical pathway that connects reactants to products. An elementary reaction is one that proceeds by a single process, such a molecular (or atomic) decomposition or a molecular collision. Typically, elementary reactions only come in **unimolecular**

$$A \rightarrow products$$

and **bimolecular**

$$A + B \rightarrow products$$

form. Occasionally, an elementary step that is **termolecular**

$$A + B + C \rightarrow products$$

(involved the simultaneous collision of three atoms or molecules) but it is generally a pair of bimolecular steps acting in rapid succession, the first forming an activated complex, and the second stabilizing that complex chemically or physically.

$$A + B \rightarrow AB^*$$

$$AB^* + C \rightarrow AB + C^*$$

The wonderful property of elementary reactions is that the **molecularity** defines the order of the rate law for the reaction step.

The Requirements of a Reaction Mechanism

A valid reaction mechanism must satisfy three important criteria:

1. The sum of the steps must yield the overall stoichiometry of the reaction.
2. The mechanism must be consistent with the observed kinetics for the overall reaction.
3. The mechanism must account for the possibility of any observed side products formed in the reaction.

Example 7.10.1:

For the reaction

$$A + B \rightarrow C$$

is the following proposed mechanism valid?

$$A + A \xrightarrow{k_1} A_2$$

$$A_2 + B \xrightarrow{k_1} C + A$$

Solution

Adding both proposed reactions gives

$$\cancel{2}\,A + \cancel{A_2} + B \rightarrow \cancel{A_2} + C + \cancel{A}$$

Canceling those species that appear on both sides of the arrow leaves

$$A + B \rightarrow C$$

which is the reaction, so the mechanism is at least stoichiometrically valid. However, it would still have to be consistent with the observed kinetics for the reaction and account for any side-products that are observed.

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7.11: The Connection between Reaction Mechanisms and Reaction Rate Laws

The great value of chemical kinetics is that it can give us insights into the actual reaction pathways (mechanisms) that reactants take to form the products of reactions. Analyzing a reaction mechanism to determine the type of rate law that is consistent (or not consistent) with the specific mechanism can give us significant insight. For example, the reaction

$$A + B \rightarrow C$$

might be proposed to follow one of two mechanistic pathways:

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{step 1}}$$

$$\underbrace{A_2 + B \xrightarrow{k_2} C}_{\text{step 2}}$$

or

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{step 1}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{step 2}}$$

The first rate law will predict that the reaction should be second order in A, whereas the second mechanism predicts that it should be first order in A (in the limit that the steady state approximation, discussed in the following sections, can be applied to A_2 and A^*). Based on the observed rate law being first or second order in A, one can rule out one of the rate laws. Unfortunately, this kind of analysis cannot confirm a specific mechanism. Other evidence is needed to draw such conclusions, such as the spectroscopic observation of a particular reaction intermediate that can only be formed by a specific mechanism.

In order analyze mechanisms and predict rate laws, we need to build a toolbox of methods and techniques that are useful in certain limits. The next few sections will discuss this kind of analysis, specifically focusing on

- the **Rate Determining Step** approximation,
- the **Steady State** approximation, and
- the **Equilibrium** approximation.

Each type of approximation is important in certain limits, and they are oftentimes used in conjunction with one another to predict the final forms of rate laws.

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7.12: The Rate Determining Step Approximation

The **rate determining step** approximation is one of the simplest approximations one can make to analyze a proposed mechanism to deduce the rate law it predicts. Simply stated, the rate determining step approximation says that a mechanism can proceed no faster than its slowest step. So, for example, if the reaction

$$A + B \rightarrow C$$

is proposed to follow the mechanism

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{slow}}$$

$$\underbrace{A_2 \xrightarrow{k_2} C + A}_{\text{fast}}$$

the rate determining step approximation suggests that the rate (expressed in terms of the appearance of product C) should be determined by the slow initial step, and so the rate law will be

$$\frac{[C]}{dt} = k_1[A]^2$$

matching the order of the rate law to the molecularity of the slow step. Conversely, if the reaction mechanism is proposed as

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{slow}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{fast}}$$

the rate determining step approximation suggests that the rate of the reaction should be

$$\frac{[C]}{dt} = k_1[A]$$

again, with the order of the rate law matching the molecularity of the rate determining step.

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7.13: The Steady-State Approximation

One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction

$$A + B \rightarrow C \tag{7.13.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{7.13.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{7.13.3}$$

The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B] \approx 0$$

or

$$[A_2] \approx \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

the above expression for $[A_2]$ can be substituted

$$\frac{d[C]}{dt} = k_2\left(\frac{k_1[A]^2}{k_2[B]}\right)[B]$$

of

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$.

Alternatively, if the mechanism for Equation 7.13.1 is proposed to be

$$A \xrightarrow{k_1} A^* \tag{7.13.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{7.13.5}$$

then the rate of change of the concentration of A^* is

$$\frac{[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds, then

$$[A^*] \approx \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\frac{d[C]}{dt} = k_2[A^*][B] \tag{7.13.6}$$

$$= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\,\cancel{[B]}}\right)\cancel{[B]} \tag{7.13.7}$$

or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

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7.14: The Equilibrium Approximation

In many cases, the formation of a reactive intermediate (or even a longer lived intermediate) involves a reversible step. This is the case if the intermediate can decompose to reform reactants with a significant probability as well as moving on to form products. In many cases, this will lead to a pre-equilibrium condition in which the **equilibrium approximation** can be applied. An example of a reaction mechanism of this sort is

$$A + B \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} AB$$

$$AB \xrightarrow{k_2} C$$

Given this mechanism, the application of the steady state approximation is cumbersome. However, if the initial step is assumed to achieve equilibrium, an expression can be found for $[AB]$. In order to derive this expression, one assumes that the rate of the forward reaction is equal to the rate of the reverse reaction for the initial step in the mechanism.

$$k_1[A][B] = k_{-1}[AB]$$

or

$$\frac{k_1[A][B]}{k_{-1}} = [AB]$$

This expression can be substituted into an expression for the rate of formation of the product C:

$$\frac{d[C]}{dt} = k_2[AB]$$

or

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}}[A][B]$$

Which predicts a reaction rate law that is first order in A, first order in B, and second order overall.

Example 7.14.1:

Given the following mechanism, apply the equilibrium approximation to the first step to predict the rate law suggested by the mechanism.

$$A + A \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} A_2$$

$$A_2 + B \xrightarrow{k_2} C + A$$

Solution

If the equilibrium approximation is valid for the first step,

$$k_1[A]^2 = k_{-1}[A_2]$$

or

$$\frac{k_1[A]^2}{k_{-1}} \approx [A_2]$$

Plugging this into the rate equation for the second step

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

yields

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}}[A]^2[B]$$

Thus, the rate law has the form

$$\text{rate} = k'[A]^2[B]$$

which is second order in A, first order in B and third order over all, and in which the effective rate constant (k' is

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

Sometimes, the equilibrium approximation can suggest rate laws that have negative orders with respect to certain species. For example, consider the following reaction

$$A + 2B \rightarrow 2C$$

A proposed mechanism for which might be

$$A + B \underset{k_1}{\overset{k_{-1},}{\rightleftharpoons}} I + C$$

$$I + B \xrightarrow{k_2} C$$

in which I is an intermediate. Applying the equilibrium approximation to the first step yields

$$k_1[A][B] = k_{-1}[I][C]$$

or

$$\frac{k_1[A][B]}{k_{-1}[C]} \approx [I]$$

Substituting this into an expression for the rate of formation of C, one sees

$$\frac{d[C]}{dt} = k_2[I][B]$$

or

$$\frac{d[C]}{dt} = \frac{k_1[A][B]}{k_{-1}[C]}[B] = \frac{k_2 k_1[A][B]}{k_{-1}[C]}$$

The rate law is then of the form

$$\text{rate} = k\frac{[A][B]^2}{[C]}$$

which is first order in A, second order in B, negative one order in C, and second order overall. Also,

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

In this case, the negative order in C means that a buildup of compound C will cause the reaction to slow. These sort of rate laws are not uncommon for reactions with a reversible initial step that forms some of the eventual reaction product.

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