CHEM-UA 652: THERMODYNAMICS AND KINETICS



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TABLE OF CONTENTS

Licensing

1: Lectures

- 1.1: Introduction, overview of thermodynamics, and the Maxwell-Boltzmann distribution
- 1.2: Ideal gas law, introduction to statistical mechanics, and the microcanonical ensemble
- 1.3: The Canonical Ensemble
- 1.4: Treating interactions - Virial coefficients
- 1.5: The van der Waals equation of state and radial distribution functions
- 1.6: Equipartitioning, Collisions, and Random Walks
- 1.7: Introduction to diffusion
- 1.8: Computational methods in statistical mechanics
- 1.9: First law of thermodynamics and thermodynamic potentials
- 1.10: Physical significance of free energy, Euler's theorem, Maxwell relations
- 1.11: Carnot engines, thermodynamic entropy, and the second and third laws
- 1.12: Introduction to the Thermodynamics of Phase Transitions
- 1.13: The Clapeyron equation, Gibbs phase rule, and Classical Nucleation Theory
- 1.14: Introduction to Solutions
- 1.15: Solution Equilibria and Colligative Properties
- 1.16: Thermochemistry
- 1.17: Chemical Equilibria
- 1.18: Introduction to Reaction Kinetics - Basic Rate Laws
- 1.19: Collision theory, transition state theory, and the prediction of rate laws and rate constants
- 1.20: Complex reaction mechanisms
- 1.21: Nonlinear kinetics and oscillating reactions
- 1.22: Kinetics of Catalysis
- 1.23: Continuously stirred tank reactors
- 1.24: Plug flow reactors and comparison to continuously stirred tank reactors

Index

Glossary

Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Lectures

1.1: Introduction, overview of thermodynamics, and the Maxwell-Boltzmann distribution
1.2: Ideal gas law, introduction to statistical mechanics, and the microcanonical ensemble
1.3: The Canonical Ensemble
1.4: Treating interactions - Virial coefficients
1.5: The van der Waals equation of state and radial distribution functions
1.6: Equipartitioning, Collisions, and Random Walks
1.7: Introduction to diffusion
1.8: Computational methods in statistical mechanics
1.9: First law of thermodynamics and thermodynamic potentials
1.10: Physical significance of free energy, Euler's theorem, Maxwell relations
1.11: Carnot engines, thermodynamic entropy, and the second and third laws
1.12: Introduction to the Thermodynamics of Phase Transitions
1.13: The Clapeyron equation, Gibbs phase rule, and Classical Nucleation Theory
1.14: Introduction to Solutions
1.15: Solution Equilibria and Colligative Properties
1.16: Thermochemistry
1.17: Chemical Equilibria
1.18: Introduction to Reaction Kinetics - Basic Rate Laws
1.19: Collision theory, transition state theory, and the prediction of rate laws and rate constants
1.20: Complex reaction mechanisms
1.21: Nonlinear kinetics and oscillating reactions
1.22: Kinetics of Catalysis
1.23: Continuously stirred tank reactors
1.24: Plug flow reactors and comparison to continuously stirred tank reactors

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1.1: Introduction, overview of thermodynamics, and the Maxwell-Boltzmann distribution

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1.2: Ideal gas law, introduction to statistical mechanics, and the microcanonical ensemble

The Ideal Gas Law

In the last lecture, we discussed the Maxwell-Boltzmann velocity and speed distribution functions for an ideal gas. Remember that, in an ideal gas, there are no interactions between the particles, hence, the particles do not exert forces on each other. However, particles do experience a force when they collide with the walls of the container. Let us assume that each collision with a wall is elastic. Let us assume that the gas is in a cubic box of length a and that two of the walls are located at $x = 0$ and at $x = a$. Thus, a particle moving along the x direction will eventually collide with one of these walls and will exert a force on the wall when it strikes it, which we will denote as F_x. Since every action has an equal and opposite reaction, the wall exerts a force $-F_x$ on the particle. According to Newton's second law, the force $-F_x$ on the particle in this direction gives rise to an acceleration via

$$-F_x = ma_x = m\frac{\Delta v_x}{\Delta t} \tag{1.2.1}$$

Here, t represents the time interval between collisions with the same wall of the box. In an elastic collision, all that happens to the velocity is that it changes sign. Thus, if v_x is the velocity in the x direction before the collision, then $-v_x$ is the velocity after, and $\Delta v_x = -v_x - v_x = -2v_x$, so that

$$-F_x = -2m\frac{v_x}{\Delta t} \tag{1.2.2}$$

In order to find Δt, we recall that the particles move at constant speed. Thus, a collision between a particle and, say, the wall at $x = 0$ will not change the particle's speed. Before it strikes this wall again, it will proceed to the wall at $x = a$ first, bounce off that wall, and then return to the wall at $x = 0$. The total distance in the x direction traversed is $2a$, and since the speed in the x direction is always v_x, the interval $\Delta t = \frac{2a}{v_x}$. Consequently, the force is

$$-F_x = -\frac{mv_x^2}{a} \tag{1.2.3}$$

Thus, the force that the particle exerts on the wall is

$$F_x = \frac{mv_x^2}{a} \tag{1.2.4}$$

The mechanical definition of pressure is

$$P = \frac{\langle F \rangle}{A} \tag{1.2.5}$$

where $\langle F \rangle$ is the average force exerted by all N particles on a wall of the box of area A. Here $A = a^2$. If we use the wall at $x = 0$ we have been considering, then

$$P = \frac{N\langle F_x \rangle}{a^2} \tag{1.2.6}$$

because we have N particles hitting the wall. Hence,

$$P = \frac{Nm\langle v_x^2 \rangle}{a^3} \tag{1.2.7}$$

from our study of the Maxwell-Boltzmann distribution, we found that

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{1.2.8}$$

Hence, since $a^3 = V$,

$$P = \frac{Nk_B T}{V} = \frac{nRT}{V} \tag{1.2.9}$$

which is the ideal gas law.

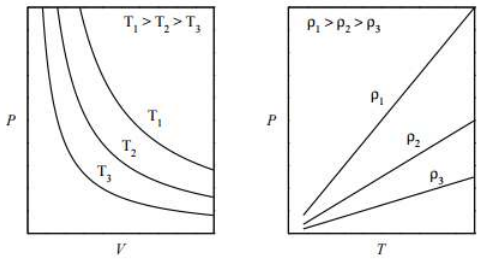


Figure 1.2.1*: (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities* $\rho = N/V$.

The ideal gas law is an example of an equation of state. One way to visualize any equation of state is to plot the so-called *isotherms*, which are graphs of P vs. V at fixed values of T . For the ideal-gas equation of state $P = nRT/V$, some of the isotherms are shown in the figure below (left panel): If we plot P vs. T at fixed volume (called the *isochores*), we obtain the plot in the right panel. What is important to note, here, is that an ideal gas can exist *only* as a gas. It is not possible for an ideal gas to condense into some kind of "ideal liquid". In other words, a phase transition from gas to liquid can be modeled only if interparticle interactions are properly accounted for.

Note that the ideal-gas equation of state can be written in the form

$$\frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} = 1 \tag{1.2.10}$$

where $\bar{V} = V/n$ is called the molar volume. Unlike V , which increases as the number of moles increases (an example of what is called an *extensive* quantity in thermodynamics), $\bar{V}$ does not exhibit this dependence and, therefore, is called *intensive*. The quantity

$$Z = \frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} \tag{1.2.11}$$

is called the *compressibility* of the gas. In an ideal gas, if we "compress" the gas by increasing P , the density ρ must increase as well so as to keep $Z = 1$. For a real gas, Z, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.

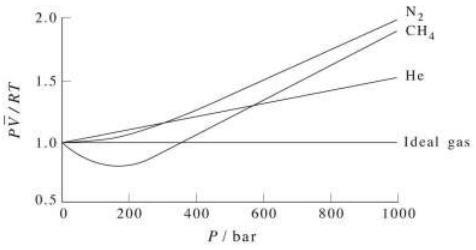


Figure 1.2.2*: Plot of the compressibility* Z *vs.* P *for several gases, together with the ideal gas, where* $Z = 1$.

Figure 1.2.2 shows a plot of Z vs. P for several real gases and for an ideal gas. The plot shows that for sufficiently low pressures (hence, low densities), each gas approaches ideal-gas behavior, as expected.

Introduction to Statistical Mechanics

Defining statistical mechanics: Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

Why do we need Statistical Mechanics:

1. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory.
2. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions.

3. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

The microscopic laws of motion

Consider a system of N classical particles. The particles a confined to a particular region of space by a "container" of volume V . In classical mechanics, the "state" of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $r_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $(v_{x_i}, v_{y_i}, v_{z_i})$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{1.2.12}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, \ldots, \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.2.13}$$

which is known as a "force field" (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.2.14}$$

where $\mathbf{F}_1, \ldots, \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we contented ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ gigabytes which is also 10^2 yottabytes! The largest computers we have today have perhaps 10^6 gigabytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}Nk_BT = \sum_{i=1}^{N} \frac{1}{2}m_i\mathbf{v}_i^2 \tag{1.2.15}$$

which can be solved to give

$$T = \frac{2}{3k_B}\left(\frac{1}{N}\sum_{i=1}^{N} \frac{1}{2}m_i\mathbf{v}_i^2\right) \tag{1.2.16}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Ensemble: Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How do we determine which thermodynamic properties characterize an ensemble?
4. How many different types of ensembles can we construct, and what distinguishes them?

Extensive and Intensive Properties in Thermodynamics

Before we discuss ensembles and how we construct them, we need to introduce an important distinction between different types of thermodynamic properties that are used to characterize the ensemble. This distinction is *extensive* and *intensive* properties.

Thermodynamics always divides the universe into a "system" and its "surroundings" with a "boundary" between them. The unity of all three of these is the thermodynamic "universe". Now suppose we allow the system to grow in such a way that both the number of particles and the volume grow with the ratio N/V remaining constant. Any property that increases as we grow the system in this way is called an *extensive* property. Any property that remains the same as we grow the system in this way is called *intensive*.

- Examples of extensive properties are N (trivially), V (trivially), energy, free energy,...
- Examples of intensive properties are pressure P, density $\rho = N/V$, molar heat capacity, temperature,....

The Microcanonical Ensemble

Consider a classical system that is completely isolated from its surroundings. Such a system has no external influences acting on it, we can restrict our discussion of the classical forces acting on the system to *conservative* forces. Conservative forces are forces that can be derived from a simple scalar function $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ by taking the negative derivative with respect to position

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \tag{1.2.17}$$

which simply means that the three components of $\mathbf{F}_i$ are generated as follows:

$$F_{x_i} = -\frac{\partial U}{\partial x_i},\ F_{y_i} = -\frac{\partial U}{\partial y_i},\ F_{z_i} = -\frac{\partial U}{\partial z_i} \tag{1.2.18}$$

The function $U(\mathbf{r}_i, \ldots, \mathbf{r}_N)$ is called the "potential" of the system or "potential energy" of the system. When this is added to the kinetic energy, we obtain the total energy \(\mathcal{E}\) as

$$\mathcal{E} = \frac{1}{2}\sum_{i=1}^{N} m_i \mathbf{v}_i^2 + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.2.19}$$

If there are *no* external fields acting on the system, then this energy is the mechanical *total internal energy*.

An isolated system will evolve in time according to Newton's second law

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.2.20}$$

Importantly, when the forces are conservative, $\mathcal{E}$ is constant with respect to time, meaning that it is conserved, and hence it is equivalent to the thermodynamic internal energy E. To see that energy conservation is obeyed, we simply need to take the derivative of $\mathcal{E}$ with respect to time and show that it is 0.

$$\mathcal{E} = \frac{1}{2}\sum_{i=1}^{N} m_i \mathbf{v}_i^2 + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.2.21}$$

$$\frac{d\mathcal{E}}{dt} = \sum_{i=1}^{N} m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i + \sum_{i=1}^{N} \frac{\partial U}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i \tag{1.2.22}$$

$$= \sum_{i=1}^{N} \dot{\mathbf{r}}_i \cdot \mathbf{F}_i - \sum_{i=1}^{N} \mathbf{F}_i \cdot \dot{\mathbf{r}}_i \tag{1.2.23}$$

$$= 0 \tag{1.2.24}$$

Since the mechanical energy is fixed, we can equate it with the thermodynamic internal energy E, which will also be fixed.

In addition to the energy, two other thermodynamic variables are trivially conserved, and they are the number of particles N, and the containing volume V. If we now imagine a collection of such systems in an ensemble, all having the same values of N, V, and E, the same underlying microscopic forces and laws of motion but all having different microscopic states, then this ensemble would be characterized by the values of N, V, and E and is called a *microcanonical ensemble*.

Entropy and the number of microscopic states

Now that we have defined one type of ensemble, the microcanonical ensemble, an important quantity pertaining to this ensemble is the number of microscopic states. For short, we will refer to "microscopic states" as "microstates". In a classical system, a microstate is simply a specification of the positions and velocities of all the particles in the system. Thus, in order to find the number of microstates, we ask the following question: In how many ways can we choose the positions and velocities for a system of N particles in a volume V and forces derived from a potential $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ such that we always obtain the same value of the energy in Equation 1.2.19? Let us denote this number as Ω, and it is clear to see that Ω is a function of N, V, and E, *i.e.*, $\Omega(N, V, E)$. Even though $\Omega(N, V, E)$ is an enormous number, the fact is that it is always finite (as opposed to infinite). How can we calculate $\Omega(N, V, E)$? In principle, $\Omega(N, V, E)$ can be computed by

$$\Omega(N, V, E) = \frac{1}{h^{3N}} \int_{E=\mathcal{E}} dx \tag{1.2.25}$$

where $\mathcal{E}$ is given by Equation 1.2.19 , E is a value for the internal energy, and $\int dx$ means integrate over all of the positions and velocities! The constant h is Planck's constant, and it accounts for the Heisenberg uncertainty principle. If all of the particles in the system are identical, then we must divide the integral on the right by a factor of $1/N!$, which accounts for the fact that the particles can be exchanged in $N!$ ways without changing the microscopic state of the system. This seemingly innocent formula is actually rather difficult to apply in practice. The number $\Omega(N, V, E)$ is an example of what is called a *partition function* in statistical mechanics. Here, $\Omega(N, V, E)$ is the partition function of the microcanonical ensemble.

The connection between the microscopic world of positions, velocities, forces, potentials, and Newtonian mechanics and the macroscopic, thermodynamic world is the entropy S, which is computed from Ω via Boltzmann's formula

$$S(N, V, E) = k_B \ln \Omega(N, V, E) \tag{1.2.26}$$

This formula was emblazoned on Boltzmann's grave, as the photograph below shows:



Figure **1.2.3 :** *Boltzmann's headstone at the Zentralfriedhof in Vienna, Austria.*

This definition of entropy also tells us something important about what entropy means. There is a commonly held (mis)conception that entropy is a measure of the degree of disorder in a system. The notion of "disorder" is certainly something that we all have an intuitive feel for (it's far easier to create chaos in your room than it is to clean it up, and it's far easier to knock over a large stack of oranges in the grocery store than it is to stack them up in the first place). However, as there is no universal definition of disorder, there is no way to quantify it, and hence, it cannot be used as a route to the entropy in a system; in fact, trying to equate entropy and disorder can even be misleading.

Common sense tells us that certain processes occur spontaneously in one direction but not in the reverse direction. But how do we distinguish between those process that truly cannot happen in reverse (such as the breaking of the glass) and those that *could* potentially happen in reverse if only we waited long enough? This thought experiment gives some idea of what entropy really measures.

Classical mechanics can actually help us understand the distinction. Recall Newton's second law of motion which describes how a system of N classical particles evolves in time:

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.2.27}$$

Let us ask what happens if we start from an initial condition $\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \mathbf{v}_1(0), \ldots, \mathbf{v}_N(0)$, evolve the system out to a time t, where we have positions and velocities $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t), \mathbf{v}_1(t), \ldots, \mathbf{v}_N(t)$, and from this point, we reverse the direction of time. Where will the system be after another time interval t has passed with the clock running backwards? We first ask what happens to Newton's second law if we reverse time in Equation 1.2.27. If we suddenly set $dt \rightarrow -dt$, the positions do not change at the moment, hence, the forces do not change either. Moreover, since $dt^2 \rightarrow dt^2$, the accelerations do not change. Thus, Newton's second law will have exactly the same form when time is reversed as then time runs in the normal forward direction. This means that the laws of motion, themselves, cannot distinguish between normal and reversed time! This condition is called *time reversal symmetry.* On the other hand, first time derivatives must change sign, hence, the velocities $\mathbf{v}_i = d\mathbf{r}_i/dt \rightarrow d\mathbf{r}_i/(-dt) = -\mathbf{v}_i$ must reverse their direction when time is reversed, hence in order to start running the clock backwards at time t, we must replace all of the velocities $\mathbf{v}_1(t), \ldots, \mathbf{v}_N(t)$ with $-\mathbf{v}_1(t), \ldots, -\mathbf{v}_N(t)$. The facts that the velocities simply change sign under time reversal but the laws of motion do not tell us that at each point in the time reversed motion, the particles will experience the same forces and, therefore, will accelerate in the same way only in the opposite direction. Thus, after another time t, the particles should end up exactly where the started, i.e., $\mathbf{r}_1(2t) = \mathbf{r}_1(0), \ldots, \mathbf{r}_N(2t) = \mathbf{r}_N(0)$. Despite this time reversal symmetry of the laws of motion (the same symmetry exists, by the way, in quantum mechanics), there seems to be a definite "arrow" of time, as many processes are truly unidirectional. A few examples will help to illustrate the point that is being made here.

Consider first a box with a partition. One half contains an ideal gas, and the other is empty. When the partition is removed, the gas will spontaneously expand to fill the box. Once the gas expands, the particles will “never”

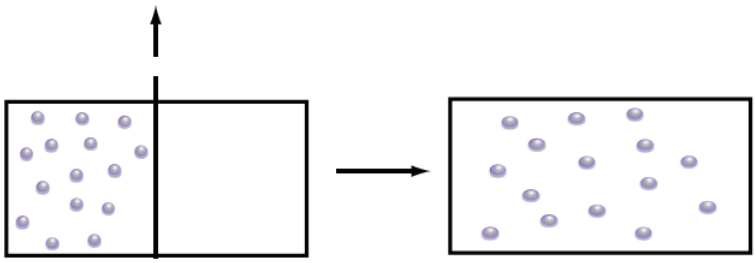


Figure 1.2.4 : *Expansion of a gas initially partitioned into one-half of its containing volume.*

spontaneously return to the left half of the box leaving the right half of the box empty, even though the process is *not* forbidden by the laws of motion or by the first law of thermodynamics. Entropy aims to quantify this tendency not captured in the first law of thermodynamics. Specifically, what entropy quantifies is the *number of available microscopic states in the system*. Hence, any thermodynamic transformation that cases the number of available microscopic states available to the system to increase will lead to an increase in entropy. While this might seem to be in contradiction to the notion that thermodynamics does not need to refer to the microscopic nature of matter, and while there is a purely thermodynamic definition of entropy that will be introduced shortly, we will see that this connection between entropy and available microstates is both fully consistent with the thermodynamic definition of entropy and intuitively very appealing as a way to understand what entropy is.

Coming back to the gas example, when the partition is in place, the volume of the system is half that of the full box. Thus, when the partition is removed, the volume doubles and the number of available microstates increases significantly. By how much? In order to see this we need to see how Ω depends on V . Recall that for an ideal gas

$$\mathcal{E} = \frac{1}{2}\sum_{i=1}^{N} m\mathbf{v}_i^2 \tag{1.2.28}$$

when all of the particles have the same mass m. Note that $\mathcal{E}$ does not depend on positions. Thus, we can write Equation 1.2.25 as

$$\Omega(N,V,E) = \frac{1}{N!h^{3N}}\left[\int_{E=\mathcal{E}} d\mathbf{x}_\mathbf{v}\right]\left[\int d\mathbf{x}_\mathbf{r}\right] \tag{1.2.29}$$

where $d\mathbf{x}_\mathbf{v}$ is the integral over velocities, and $d\mathbf{x}_\mathbf{r}$ is the integral over positions. All we need to do is look at the latter to see how Ω depends on the volume. Suppose the gas occupies a cube of side length a with faces at $x = 0$, $x = a$, $y = 0$, $y = a$, $z = 0$, and at $z = a$. Then, since we have N particles, and we have to integrate over the positions of all of them, we need to integrate each position over the spatial domain defined by this box:

$$\int d\mathbf{x}_\mathbf{r} = \left[\int_0^a dx_1 \int_0^a dy_1 \int_0^a dz_1\right] \ldots \left[\int_0^a dx_N \int_0^a dy_N \int_0^a dz_N\right] \tag{1.2.30}$$

This means that we have $3N$ integrals that are all exactly the same. Hence, we can write this as

$$\int d\mathbf{x}_\mathbf{r} = \left[\int_0^a dx_1\right]^{3N} \tag{1.2.31}$$

or

$$\int d\mathbf{x}_\mathbf{r} = a^{3N} = V^N \tag{1.2.32}$$

and therefore, $\Omega(N,V,E) \propto V^N$

Thus, the ratio of available states after the partition is removed to that before the partition is removed is $(2V/V)^N = 2^N$. As we will see shortly, this is equivalent to increase in entropy by $N \ln 2$. Hence, in this thought experiment, entropy increases when the

partition is removed because the number of microscopic states increases.

Let us now contrast this thought experiment with another one that differs from the first in one subtle but key respect. Let us suppose that we are somehow able to collect of the gas particles into the left half of the box without having to employ a partition. The situation is shown in the figure below. After the particles are thus collected, we allow them to evolve naturally according to the laws of motion, and not unexpectedly, this evolution causes them to fill the box, and we never observe them to return to the initial state in which they were prepared. Does the entropy increase in this case? No! Even though it might seem that the system evolves from a (relatively) ordered state to one with greater disorder, the number of microscopic states remains the same throughout the expansion. What distinguishes this case from the previous one is that here, we create a highly unlikely initial state without the use of a device that restricts the number of available states. How unlikely is this initial state? That is, what is the probability that it would occur spontaneously given the total number of available microstates? This probability is given by the fraction of microscopic states represented by the gas occupying half the box to that of the gas occupying the full volume of the box. For an ideal gas, this ratio is $(V/2V)^N = (1/2)^N$. Hence, if $N \sim 10^{23}$, the probability is so small that one would need to wait a time equal to many, many times the current lifetime of the universe to see it happen, even though it is not forbidden by the laws of motion. Even if $N = 100$, the probability is still on the order of 10^{-30}, which is negligible. Even though entropy does not increase, we still observe this process as “one way” because the numberof states in which the gas fills the volume of the box compared to the number of states in which it spontaneously occupies just one half of it, is so astronomically large that it can never find its way to one of the extremely unlikely states in which the particles aggregate into just one half of the box.

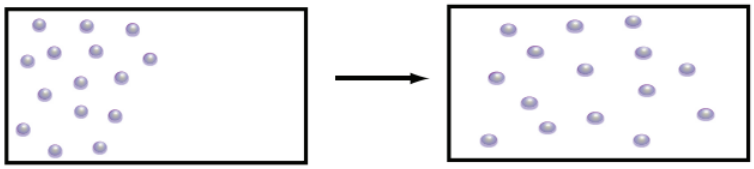


Figure **1.2.5** *: Expansion of a gas initially located in one-half of its containing volume.*

An important consequence of Boltzmann’s formula is that it proves entropy is an additive quantity, which is always assumed to be true in thermodynamics. Let us consider two independent systems, denoted A and B, and let Ω_A be the number of microstates associated with system A, and let Ω_B be the number of microstates associated with system B. The number of microstates associated with the combined system $A + B$ is then the product $\Omega_{A+B} = \Omega_A \Omega_B$. But what is the entropy of the combined system?

$$\begin{aligned} S_{A+B} &= k_B \ln \Omega_{A+B} = k_B \ln (\Omega_A \Omega_B) \\ &= k_B \ln \Omega_A + k_B \ln \Omega_B \\ &= S_A + S_B \end{aligned} \tag{1.2.33}$$

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1.3: The Canonical Ensemble

The Canonical Ensemble

In the microcanonical ensemble, the common thermodynamic variables are N, V, and E. We can think of these as "control" variables that we can "dial in" in order to control the conditions of an experiment (real or hypothetical) that measures a set of properties of particular interest.

However, when we go into the lab, we never "dial in" a particular energy E for the system. Generally, we can fix external parameters such as temperature T or pressure P (or both), but the energy is a quantity to which we simply do not have direct access. For this reason, the microcanonical ensemble is often not the ensemble of choice for performing calculations using statistical mechanics, particularly if one wishes to mimic as closely as possible the conditions of an experiment. In addition, the integral form of the partition function

$$\Omega(N,V,T) = \frac{1}{h^{3N}} \int_{\mathcal{E}(x)=E} dx \tag{1.3.1}$$

is difficult to use because of the restriction that the mechanical energy $\mathcal{E}(x)$ be fixed at a chosen value E for the total internal energy.

The first ensemble we will consider that attempts to capture more closely the conditions of an experiment is the so-called *canonical* ensemble, which is characterized by the thermodynamic variables N, V, and T. In order to fix the temperature, however, we must have a mechanism to inject heat into the system and extract heat from it in order to regulate the average kinetic energy. This means that the total energy is no longer conserved, as the system must interact with the environment in order to effect this heat exchange.

Conceptually, we imagine that our system interacts with a very large heat source, called a *thermal reservoir*. The thermal reservoir is also a mechanical system, albeit an extremely large one, with an internal energy E_r and having N_r particles in a volume V_r. However, since N_r and V_r do not change, we only need to consider how the energy E_r of the reservoir changes as the energy E of the system changes. The combination of system + reservoir comprises the thermodynamic universe, which is a microcanonical system (after all, it is isolated from any additional surroundings) having a fixed total energy E_T. Since $N_r \gg N$, it follows that $E_r \gg E$.

The total energy $E_T = E + E_r$. Although E_T is fixed, both E and E_r fluctuate, and this means that the systems are not independent. Thus, if we ask how many microstates are available to the combined system + reservoir, which we will denote $\Omega_T(N_T, V_T, E_T)$, where $N_T = N + N_r$ and $V_T = V + V_r$, we see that we cannot write this as a simple product of $\Omega(N,V,E)\Omega_r(N_r,V_r,E_r)$. In what follows, since N, N_r, V, and V_r never change, we will suppress the dependence of Ω on these and just show the energy dependence. The correct expression for $\Omega_T(E_T)$ is

$$\Omega_T(E_T) = \int_0^{E_T} \Omega(E)\Omega_r(E_T - E)dE \tag{1.3.2}$$

since $E_r = E_T - E$. On the other hand, if we are interested in the number of states available to the system at a particular energy E, then we can use the simple product formula and write this number, $\Omega(E)$, as a ratio:

$$\Omega(E) = \frac{\Omega_T(E_T)}{\Omega_r(E_T - E)} \tag{1.3.3}$$

The more relevant quantity study is the actual thermodynamic observable, which is the entropy $S(E)$ of the system. This is given by

$$\begin{aligned} S(E) &= k_B \ln \Omega(E) = k_B \ln \Omega_T(E_T) - k_B \ln \Omega_r(E_T - E) \\ &= S_T(E_T) - S_r(E_T - E) \end{aligned} \tag{1.3.4}$$

We now exploit the fact that the reservoir is much larger than the system and perform a Taylor expansion up to first order in the system energy. This is justified as $E \ll E_T$. To first order,

$$S_r(E_T - E) \approx S_r(E_T) - \left(\frac{\partial S_r}{\partial E_r}\right)_{E_r = E_T} E \tag{1.3.5}$$

Since E_T is fixed, and $E_T = E + E_r$, if the energy of the thermal reservoir change by a small amount dE_r, the system's energy must change by an equal and opposite amount, i.e., $dE = -dE_r$. Consequently, we can write

$$S_r(E_T - E) \approx S_r(E_T) + \left(\frac{\partial S_r}{\partial E}\right)_{E_r = E_T} E \tag{1.3.6}$$

The only thing we still need to do is evaluate the derivative $\partial S_r / \partial E$. Thermodynamics posits that heat is a form of energy. If this postulate is correct, then when N and V remain fixed, any change in energy of the system or reservoir must be due to a transfer of heat dQ between the two. Since energy is a state function, how this heat is transferred is irrelevant to the actual energy change we observe, so let us suppose that the transfer is carried out reversibly. Designating the heat transfer as dQ_{rev}, the energy change dE must equal this heat transfer:

$$dE = dQ_{\text{rev}} \tag{1.3.7}$$

(We will later see that this is in agreement with the first law of thermodynamics.) The thermodynamic definition of entropy then can be used to express dQ_{rev} as

$$dQ_{\text{rev}} = T dS_r \tag{1.3.8}$$

where dS_r is the change in entropy of the reservoir as a result of the heat transfer at temperature T. Rearranging this, we find that the temperature is given by

$$\frac{1}{T} = \left(\frac{\partial S_r}{\partial E}\right)_{N_r, V_r} \tag{1.3.9}$$

However, since the system and reservoir are in thermal equilibrium, they must have the same temperature. Thus, it follows that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \tag{1.3.10}$$

Interestingly, we see that we can also use the partition function to determine the temperature

$$\frac{1}{T} = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \tag{1.3.11}$$

which is our first example of how the partition function is used to compute a thermodynamic property! It's also our first illustration of how we start with a purely microscopic description of the system and arrive at a thermodynamic observable.

Now using this relation for temperature in our Taylor expansion, we find

$$S_r(E_T - E) \approx S_r(E_T) + \frac{E}{T} \tag{1.3.12}$$

Therefore,

$$S(E) = S_T(E_T) - S_r(E_T) - \frac{E}{T} \tag{1.3.13}$$

Taking the exponential of both sides, we finally recover the number of states available to the system when it is in contact with a thermal reservoir:

$$\Omega(E) = e^{S(E)/k_B} = C e^{-E/k_B T} \tag{1.3.14}$$

where C is a constant.

Of course, what we are really interested in is the number of microstates, as specified by the coordinates and momenta, designated as x, when the system is in contact with a thermal reservoir. However, Equation 1.3.14 immediately tells us what the probability distribution of x needs to be. If we identify the thermodynamic energy E with the mechanical energy $\mathcal{E}(x)$, then this distribution is given by

$$f(x) = C e^{-\mathcal{E}/k_B T} = C e^{-\beta \mathcal{E}(x)} \tag{1.3.15}$$

The mechanical energy is given by

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.3.16}$$

$$= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.3.17}$$

where the fact that the momentum $\mathbf{p}_i = m_i \mathbf{v}_i$ has been used. Written in this way, we also see that the mechanical energy $\mathcal{E}(x)$ is also the *Hamiltonian* $\mathcal{H}(x)$. Here, we see that the constant C can be determined by normalization of the distribution function

$$C = \frac{1}{Q(N,V,T)} \tag{1.3.18}$$

$$Q(N,V,T) = \frac{1}{h^{3N}} \int e^{-\mathcal{E}(x)/k_B T} dx = \frac{1}{h^{3N}} \int e^{-\beta \mathcal{H}(x)} dx \tag{1.3.19}$$

The quantity $Q(N,V,T)$ is, thus, a measure of the number of microstates available to the system and is, therefore, the partition function of the canonical ensemble. If the N particles in the system are all identical, then we need the additional combinatorial factor of $1/N!$ in the definition of Q, and we write

$$Q(N,V,T) = \frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{E}(x)} dx = \frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{H}(x)} dx \tag{1.3.20}$$

Clearly, there are analogous factors when the system contains N_A particles of type A, N_B particles of type B,...

A few comments are in order at this point. First, we immediately see that if there are no interactions in the system, i.e., $U = 0$, then the canonical distribution function becomes the Maxwell-Boltzmann distribution function

$$f(x) = \frac{1}{Q} e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2/2m_i} = \frac{1}{Q} e^{-\beta \sum_{i=1}^{N} m_i \mathbf{v}_i^2/2} \tag{1.3.21}$$

which is the appropriate canonical distribution for an ideal gas.

A second important point concerns the fact that the energy is a sum of purely momentum-dependent terms and a purely position dependent term:

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.3.22}$$

Given this, the partition function always separates into a product of two integrals:

$$Q(N,V,T) = C_N \left[\int e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2/2m_i} d\mathbf{x}_\mathbf{p} \right] \left[\int e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} d\mathbf{x}_\mathbf{r} \right] \tag{1.3.23}$$

$$= C_N \left[\int e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2/2m_i} d\mathbf{p}_1 \ldots d\mathbf{p}_N \right] \left[\int e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} d\mathbf{r}_1 \ldots \mathbf{r}_N \right] \tag{1.3.24}$$

Importantly, note that the first integral is *always* the same for any system, and in fact, it is just the ideal-gas partition function, which we will work out shortly. The second part, involving the potential energy $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the only 4 part that is different for different systems. In fact, this is the only part of the partition function that is interesting, as it is particular to each individual system and is what gives rise to the particular properties of that system!

A third important point concerns the use of the canonical distribution to compute averages. Let A be some equilibrium property of our system, e.g., temperature, pressure, free energy,..., and let $a(x)$ be some function of the coordinates and momenta whose average over an ensemble yields the property A. An example is the use of the kinetic energy to obtain temperature. In this example, the property A is the temperature T and the function $a(x)$ is the kinetic energy $a(x) = (2/3nR) \sum_{i=1}^{N} \mathbf{p}_i^2/2m_i$. The relation between A and $a(x)$ is

$$A = \langle a(x) \rangle = \int f(x)\, a(x)\, dx = \frac{C_N}{Q(N,V,T)} \int a(x)\, e^{-\beta \mathcal{E}(x)} dx \tag{1.3.25}$$

where $C_N = 1/h^{3N}$ if all the particles are distinguishable or $C_N = 1/N! h^{3N}$ if they are indistinguishable.

Thermodynamics From the Partition Function

Total internal energy

In the canonical ensemble, the mechanical energy of the system does is not conserved but rather fluctuates due to the exchange of heat between it and the thermal reservoir. Thus, if we want to compute the total internal energy, we must perform an average of $\mathcal{E}(x)$ over the ensemble. Using the rule in Equation 1.3.25, we would compute the energy as

$$E = \frac{C_N}{Q(N,V,T)} \int \mathcal{E}(x)\, e^{-\beta \mathcal{E}(x)} dx \tag{1.3.26}$$

Note, however, that we can write

$$\mathcal{E}(x)\, e^{-\beta \mathcal{E}(x)} = -\frac{\partial}{\partial \beta} e^{-\beta \mathcal{E}(x)} \tag{1.3.27}$$

Therefore,

$$E = -\frac{C_N}{Q(N,V,T)} \int \frac{\partial}{\partial \beta} e^{-\beta \mathcal{E}(x)} \tag{1.3.28}$$

$$= -\frac{1}{Q(N,V,T)} \frac{\partial}{\partial \beta} C_N \int e^{-\beta \mathcal{E}(x)} \tag{1.3.29}$$

$$= -\frac{1}{Q(N,V,T)} \frac{\partial}{\partial \beta} Q(N,V,T) \tag{1.3.30}$$

$$= -\frac{\partial}{\partial \beta} \ln Q(N,V,T) \tag{1.3.31}$$

Of course, $Q(N,V,T)$ is as much a function of β as it is a function of T since $\beta = 1/k_B T$.

Heat capacity at constant volume

The heat capacity at constant volume, denoted C_V, is defined to be the change in thermodynamic energy with respect to temperature:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \tag{1.3.32}$$

Since

$$E = -\frac{\partial}{\partial \beta} \ln Q(N,V,\beta) \tag{1.3.33}$$

we see that

$$C_V = \frac{\partial E}{\partial T} \tag{1.3.34}$$

$$= \frac{\partial E}{\partial \beta} \frac{\partial \beta}{\partial T} \tag{1.3.35}$$

$$= \frac{1}{k_B T^2} \frac{\partial^2}{\partial \beta^2} \ln Q(N,V,\beta) \tag{1.3.36}$$

$$= k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Q(N,V,\beta) \tag{1.3.37}$$

Pressure

Let us consider a simple thought experiment, which is illustrated in the figure below: A system of N particles is

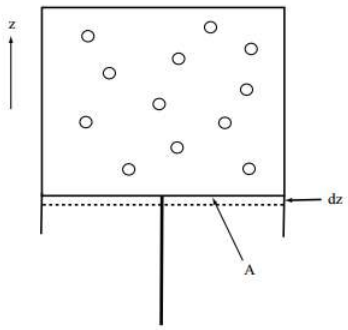


Figure 3.1: *Illustration of a thought experiment in which a system is compressed via a piston pushed into the system along the positive z axis.*

compressed by a piston by pushing the piston in the positive z direction. Since this is a classical thought experiment, we think in terms of forces. The piston exerts a constant force of magnitude F on the system. The direction of the force is purely in the positive z direction, so that we can write the force vector $\mathbf{F}$ as $\mathbf{F} = (0, 0, F)$. The system exerts an equal and opposite force on the piston of the form $(0, 0, -F)$. If the energy of the system is E, then the force exerted by the system on the piston will be given by the negative change in E with respect to z:

$$-F = -\frac{dE}{dz} \tag{1.3.38}$$

or

$$F = \frac{dE}{dz} \tag{1.3.39}$$

The force exerted by the system on the piston is manifest as an observable pressure P equal to the force F divided by the area A of the piston, $P = F/A$. Given this, the observed pressure is just

$$P = \frac{dE}{Adz} \tag{1.3.40}$$

Since the volume decreases when the system is compressed, we see that $Adz = -dV$. Hence, we can write the pressure as $P = -dE/dV$.

Of course, the relation $P = -dE/dV$ is a thermodynamic one, but we need a function of x that we can average over the ensemble. The most natural choice is

$$p(x) = -\frac{d\mathcal{E}(x)}{dV} \tag{1.3.41}$$

so that $P = \langle p(x) \rangle$. Setting up the average, we obtain

$$P = -\frac{C_N}{Q(N,V,T)} \int \frac{\partial \mathcal{E}}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{1.3.42}$$

$$= \frac{C_N}{Q(N,V,T)} \frac{1}{\beta} \int \frac{\partial}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{1.3.43}$$

$$= \frac{k_B T}{Q(N,V,T} \frac{\partial}{\partial V} C_N \int e^{-\beta \mathcal{E}(x)} \tag{1.3.44}$$

$$= k_B T \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right) \tag{1.3.45}$$

Isothermal Compressibility

Recall from the last problem set that the isothermal compressibility is given by

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_T^{-1} \tag{1.3.46}$$

From Equation ???, we can easily see that the isothermal compressibility can be expressed in terms of the partition function as

$$\kappa_T = -\frac{1}{Vk_BT}\left(\frac{\partial^2}{\partial V2}\ln Q(N,V,\beta)\right)^{-1} \tag{1.3.47}$$

Ideal Gas in the Canonical Ensemble

Recall that the mechanical energy for an ideal gas is

$$\mathcal{E}(x) = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m} \tag{1.3.48}$$

where all particles are identical and have mass m. Thus, the expression for the canonical partition function $Q(N,V,T)$:

$$Q(N,V,T) = \frac{1}{N!h^{3N}}\int dx\, e^{-\beta\sum_{i=1}^{N}\mathbf{p}_i^2/2m} \tag{1.3.49}$$

Note that this can be expressed as

$$Q(N,V,T) = \frac{1}{N!h^{3N}}V^N\left[\int dp\, e^{-\beta p^2/2m}\right]^{3N} \tag{1.3.50}$$

Evaluating the Gaussian integral gives us the final result immediately:

$$Q(N,V,T) = \frac{1}{N!}\left[\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\right]^N \tag{1.3.51}$$

The expressions for the energy

$$E = -\frac{\partial}{\partial\beta}\ln Q(N,V,T) \tag{1.3.52}$$

which give

$$E = \frac{3}{2}Nk_BT = \frac{3}{2}nRT \tag{1.3.53}$$

and pressure

$$P = k_BT\left(\frac{\partial\ln Q(N,V,T)}{\partial V}\right) \tag{1.3.54}$$

give

$$P = \frac{Nk_BT}{V} = \frac{nRT}{V} \tag{1.3.55}$$

which is the ideal gas law.

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1.4: Treating interactions - Virial coefficients

The Isothermal-Isobaric Ensemble

The isothermal-isobaric ensemble is the closest mimic to the conditions under which most experiments are performed, namely under conditions of constant N, P, and T. In order to fix the pressure and temperature, the system must allowed to exchange heat with its surrounds, and the surrounds must also act as a kind of isotropic "piston" on the system, allowing the system's volume V to fluctuate in response to an applied pressure P. If the volume fluctuates, then we can treat is as an additional mechanical variable in the system. If this is the case, then the energy E can change in response to the exchange of heat, while there is an additional energy term $P\Delta V$, which when added to the energy change ΔE, gives the total energy change in response to both the piston and the heat exchange. This sum $\Delta E + P\Delta V$ goes by the name "enthalpy" and is denoted ΔH:

$$\Delta H = \Delta E + P\Delta V \tag{1.4.1}$$

The mechanical version of this simply replaced E by the mechanical energy $\mathcal{E}(x)$, and we would integrate a Boltzmann distribution of $\mathcal{E}(x) + PV$ over all coordinates, momenta, and volumes in order to produce a partition function:

$$\Delta(N,P,T) = C_N \int_0^\infty dV \int dx\, e^{-\beta(\mathcal{E}(x)+PV)} \tag{1.4.2}$$

$$= \int_0^\infty dV e^{-\beta PV} C_N \int dx\, e^{-\beta\mathcal{E}(x)} \tag{1.4.3}$$

$$= \int_0^\infty dV e^{-\beta PV} Q(N,V,T) \tag{1.4.4}$$

The last line of this shows that there is a very simple relation between the canonical partition function and that of the isothermal-isobaric ensemble. Once we know the canonical partition function, we just need to do one volume integral in order to determine the partition function of the isothermal-isobaric ensemble. The thermodynamic relations are also completely analogous to those of the canonical ensemble. Thus, the average enthalpy H is given by

$$H = -\frac{\partial}{\partial\beta} \ln \Delta(N,P,T) \tag{1.4.5}$$

and the constant-pressure heat capacity C_P becomes

$$C_P = k_B\beta^2 \frac{\partial^2}{\partial\beta^2} \ln \Delta(N,P,T) \tag{1.4.6}$$

The only real difference from the canonical ensemble is that we determine an average volume V from the pressure derivative of $\Delta(N,P,T)$:

$$V = -k_B T \frac{\partial}{\partial P} \ln \Delta(N,P,T) \tag{1.4.7}$$

Treating Interactions: Virial Coefficients

We have seen that if we can determine a canonical partition function, then we can also easily compute the properties of a system at constant pressure by simply applying Equation 4.2. But how can we compute a canonical partition function for a system in which there are real interactions present?

One way is to use computer simulation techniques. If we run a molecular dynamics or Monte Carlo calculation, then, in addition to approximating the actual microscopic motion of a system, we are, in effect, using the simulation to "do 2 the many-dimensional integrals" over coordinates and momenta! Of course, the downside of this is that computer simulations can be time consuming, and they only allow us to examine one thermodynamic state point at a time. Each new state point is a new simulation. In addition, the computer will spit out reams of data, and we have, somehow, to make sense of it all. As the Hungarian-American physicist and Nobel laureate, Eugene Wigner once said, "It is nice to know that the computer understands the problem, but I would like to

understand it too". For this reason, analytical techniques can play an extremely valuable role, as they provide insights that cannot be easily gleaned from computer simulations.

Let us start, therefore, by considering a gas at low density and compute the canonical partition function for this system. We will assume that the density is sufficiently low that each particle interacts with just one other particle at a time (which would certainly not be the case in a liquid or solid). Because there interactions are pair-wise, we can assume that the potential energy is a sum of pair-wise terms:

$$U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|) \tag{1.4.8}$$

A typical plot of such a potential and the force it produces between two particles is shown in Figure 4.1. However, if each particle interacts with just one other particle at a time, then we can simplify the complicated sums above and write the potential as

$$U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = u(|\mathbf{r}_1 - \mathbf{r}_2|) + u(|\mathbf{r}_3 - \mathbf{r}_4|) + \ldots u(|\mathbf{r}_{N-1} - \mathbf{r}_N|) \tag{1.4.9}$$

provided that we recognize this as being just one possible way we can pair up the particles. If we account for all possible ways we can do this as a combinatorial factor in the counting of microstates, then we have all of the information we need to construct the partition function.

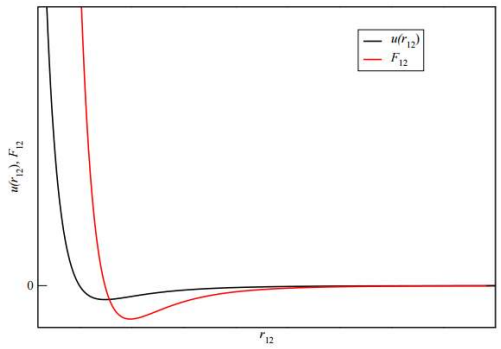


Figure 4.1: Typical potential energy and force curves for two particles in a real gas.

So let's see how we can do this. Consider, first, the case of just four particles. In how many ways can we pair them up so that each particle interacts with just one other? There are, in fact, three possibilities. We have, for example, $(1,2)(3,4)$, but we also have $(1,3)(2,4)$, and $(1,4)(2,3)$. Note that the case $(1,2)(3,4)$ corresponds to what we have written in Equation 4.6. That is, for this pairing, we would write the potential as $U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = u(|\mathbf{r}_1 - \mathbf{r}_2|) + u(|\mathbf{r}_3 - \mathbf{r}_4|)$. The three possibilities can be expressed as $\mathbf{3 \cdot 1}$.

Now suppose we had six particles. In how many ways can we pair these up. If you enumerate them all, you'll find that there are 15 possibilities:

$$(1,2)(3,4)(5,6)$$
$$(1,2)(3,5)(4,6)$$
$$(1,2)(3,6)(4,5)$$

$$(1,3)(2,4)(5,6)$$
$$(1,3)(2,5)(4,6)$$
$$(1,3)(2,6)(4,5)$$

$$(1,4)(2,3)(5,6)$$
$$(1,4)(2,5)(3,6)$$
$$(1,4)(2,6)(3,5)$$

$$(1,5)(2,3)(4,6)$$
$$(1,5)(2,4)(3,6)$$
$$(1,5)(2,6)(3,4)$$

$$(1,6)(2,3)(4,5)$$
$$(1,6)(2,4)(3,5)$$
$$(1,6)(2,5)(3,4)$$

Note that $15 = 5 \cdot 3 \cdot 1$. Thus, in general, if we have N particles, where N must be even so that we can pair them up, then the number of ways we can pair them up is $(N-1)(N-3)(N-5)\ldots = (N-1)!!$.

Recall that the canonical partition function is

$$Q(N,V,T) = C_N \int d\mathbf{x}_\mathbf{p}\, e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2/2m} \int d\mathbf{x}_\mathbf{r}\, e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{1.4.10}$$

Let us denote by $Z(N,V,T)$

$$Z(N,V,T) = \int d\mathbf{r}_1 \ldots d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{1.4.11}$$

We will be interested in computing the equation of state for our system, which we obtain by computing the pressure from

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right) \tag{1.4.12}$$

However, $Z(N,V,T)$ contains all of the volume dependence of Q, so we really only need to worry about it, and the pressure would then be given by

$$P = k_B T \left(\frac{\partial \ln Z}{\partial V}\right) \tag{1.4.13}$$

In the limit that we can consider each particle as interacting with just one other particle at a time, for which there are $(N-1)!!$ possible combinations, we can write Z as

$$Z(N,V,T) = (N-1)!! \int d\mathbf{r}_1 \cdots d\mathbf{r}_N\, e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)}\, e^{-\beta u(|\mathbf{r}_3-\mathbf{r}_4|)} \ldots\, e^{-\beta u(|\mathbf{r}_{N-1}-\mathbf{r}_N|)} \tag{1.4.14}$$

$$= (N-1)!! \left[\int d\mathbf{r}_1\, d\mathbf{r}_2\, e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)}\right] \left[\int d\mathbf{r}_3\, d\mathbf{r}_4\, e^{-\beta u(|\mathbf{r}_3-\mathbf{r}_4|)}\right] \tag{1.4.15}$$
$$\cdots \left[\int d\mathbf{r}_{N-1}\, d\mathbf{r}_N\, e^{-\beta u(|\mathbf{r}_{N-1}-\mathbf{r}_N|)}\right]$$

All of the integrals in the brackets are exactly the same. Moreover, for N particles, there are $N/2$ pairs we can make, so we can write the above expression as

$$Z(N,V,T) = (N-1)!! \left[\int d\mathbf{r}_1\, d\mathbf{r}_2\, e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)}\right]^{N/2} \tag{1.4.16}$$

Next, let's look at the prefactor of $(N-1)!!$. Recall that $N! = N(N-1)(N-2)\cdots 1$. This is a product of N terms, and if N is $N! \approx N^N e^{-N}$, which is known as Sterling's approximation. Similarly for $(N-1)!! = (N-1)(N-3)\cdots 3 \cdot 1$, the leading term is $N-1$

$\approx N$, and there are $N/2$ terms in the product, so the approximation for a double factorial when N is large becomes $(N-1)!! \approx N^{N/2}e^{-N/2}$. Thus, we can write Z as

$$Z(N,V,T) \approx e^{-N/2}\left[N\int d\mathbf{r}_1\, d\mathbf{r}_2\, e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)}\right]^{N/2} \tag{1.4.17}$$

In fact, the $e^{-N/2}$ we can simply absorb into the C_N in the definition of Q, as it is volume independent and will not affect anything our calculations. Thus, it is sufficient for us to consider simply

$$Z(N,V,T) \approx \left[N\int d\mathbf{r}_1\, d\mathbf{r}_2\, e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)}\right]^{N/2} \tag{1.4.18}$$

In order to simplify the integral, let us change variables to

$$\mathbf{R} = \tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2), \quad \mathbf{r} = \mathbf{r}_1-\mathbf{r}_2 \tag{1.4.19}$$

for which $d\mathbf{r}_1 d\mathbf{r}_2 = d\mathbf{R}d\mathbf{r}$. Substituting this in, we obtain

$$Z(N,V,T) \approx \left[N\int d\mathbf{R}\, d\mathbf{r}\, e^{-\beta u(|\mathbf{r}|)}\right]^{N/2} \tag{1.4.20}$$

Since the integrand does not depend on $\mathbf{R}$, we can easily integrate over $\mathbf{R}$:

$$\int d\mathbf{R} = \int_0^a dX \int_0^a dY \int_0^a dZ = a^3 = V \tag{1.4.21}$$

Then

$$Z(N,V,T) = V^{N/2}\left[N\int d\mathbf{r}\, e^{-\beta u(|\mathbf{r}|)}\right]^{N/2} \tag{1.4.22}$$

The remaining integral still has an implied volume dependence in the sense that

$$\int d\mathbf{r}\, e^{-\beta u(|\mathbf{r}|)} = \int_0^a dx \int_0^a dy \int_0^a dz\, e^{-\beta u(|\mathbf{r}|)}$$

In order to make this volume dependence easier to work with, we go into a set of scaled coordinates

$$\mathbf{s} = \frac{\mathbf{r}}{a} = \frac{\mathbf{r}}{V^{1/3}} = V^{-1/3}\mathbf{r} \tag{1.4.23}$$

The components of $\mathbf{s}$ all lie in the interval $[0,1] : s_x \in [0,1], s_y \in [0,1], s_z \in [0,1]$. Moreover, $d\mathbf{r} = dx\, dy\, dz = a^3 ds_x\, ds_y\, ds_z = V d\mathbf{s}$. Putting this into the partition function, we have

$$Z(N,V,T) = V^{N/2}\left[NV\int d\mathbf{s}\, e^{-\beta u(|v^{1/3}\mathbf{s}|)}\right]^{N/2} \tag{1.4.24}$$

$$= V^N\left[N\int d\mathbf{s}\, e^{-\beta u(|V^{1/3}\mathbf{s}|)}\right]^{N/2} \tag{1.4.25}$$

This is now an expression we can differentiate with respect to V to obtain the pressure. Using Equation 4.11, we find

$$P = k_BT\frac{\partial}{\partial V}\left\{\ln V^N + \ln\left[N\int d\mathbf{s}\, e^{-\beta u(|V^{1/3}\mathbf{s}|)}\right]^{N/2}\right\} \tag{1.4.26}$$

$$= k_BT\frac{\partial}{\partial V}\left\{N\ln V + \frac{N}{2}\ln\left[N\int d\mathbf{s}\, e^{-\beta u(|V^{1/3}\mathbf{s}|)}\right]\right\} \tag{1.4.27}$$

$$= \frac{Nk_BT}{V} + k_BT\frac{\partial}{\partial V}\left\{\frac{N}{2}\ln\left[N\int d\mathbf{s}\, e^{-\beta u(|V^{1/3}\mathbf{s}|)}k\right]\right\} \tag{1.4.28}$$

Let

$$I(V) = \int d\mathbf{s}\, e^{-\beta u(|V^{1/3}\mathbf{s}|)} \tag{1.4.29}$$

If we assume that the interaction is a small perturbation to ideal-gas behavior, then we can take $I(V)$ to be a small quantity. In fact, we will see below that because $dI/dV \sim 1/V^2$, $I(V) \sim 1/V$, and since $1/V \sim 1/N$, $I(V) \sim 1/N$. In this case, $NI(V) \sim 1$, and we can use the approximation $\ln(1+x) \approx x$ to write

$$\ln NI(V) = \ln(1 + NI(V) - 1) \approx (NI(V) - 1) \tag{1.4.30}$$

so that

$$P = \frac{Nk_BT}{V} + \frac{Nk_BT}{2}\frac{\partial}{\partial V}(NI(V) - 1) = \frac{Nk_BT}{V} + \frac{N^2k_BT}{2}\frac{\partial I}{\partial V} \tag{1.4.31}$$

Let's now look at the volume derivative of $I(V)$. Applying the chain rule, we have

$$\frac{\partial I}{\partial V} = -\beta \int d\mathbf{s} \frac{\partial u}{\partial (V^{1/3}\mathbf{s})} \cdot \mathbf{s}\frac{1}{3}V^{-2/3}e^{-\beta u(|V^{1/3}\mathbf{s}|)} \tag{1.4.32}$$

Now that we've taken the volume derivative, we can go back to unscaled coordinates via $\mathbf{s} = V^{-1/3}\mathbf{r}$. Remember $d\mathbf{s} = (1/V)d\mathbf{r}$. If we do this, then the integral looks much less ugly:

$$\frac{\partial I}{\partial V} = -\frac{\beta}{3V^2}\int d\mathbf{r}\frac{\partial u}{\partial \mathbf{r}} \cdot \mathbf{r}\, e^{-\beta u(|\mathbf{r}|)} \tag{1.4.33}$$

The term appearing in the integrand

$$\mathbf{r}\frac{\partial u}{\partial \mathbf{r}}$$

comes up frequently in classical mechanics and is called the *virial*. Recognizing that $u(|\mathbf{r}|)$ is a function of $r = |\mathbf{r}|$, which is just the length of the vector $\mathbf{r}$, it follows that

$$\frac{\partial u}{\partial \mathbf{r}} = \frac{du}{dr}\frac{\partial r}{\partial \mathbf{r}} \tag{1.4.34}$$

$$= \frac{du}{dr}\frac{\mathbf{r}}{r} \tag{1.4.35}$$

so that

$$\mathbf{r} \cdot \frac{\partial u}{\partial \mathbf{r}} = \frac{\partial u}{\partial r}\mathbf{r} \cdot \frac{\mathbf{r}}{r} = r\frac{du}{dr} \tag{1.4.36}$$

Thus,

$$\frac{\partial I}{\partial V} = -\frac{\beta}{3V^2}\int d\mathbf{r}\, r\frac{du}{dr}e^{-\beta u(r)} \tag{1.4.37}$$

Now transform to spherical polar coordinates in $\mathbf{r}$, which gives

$$\frac{\partial I}{\partial V} = -\frac{\beta}{3V^2}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr\, r^3 \frac{du}{dr}e^{-\beta u(r)} \tag{1.4.38}$$

Note that we have made the approximation that the r integral can be taken from 0 to ∞. Strictly speaking, this is wrong because this integral should be limited by the maximum r allowed by the containing volume. However, as Figure 4.1 indicates, $u'(r) = \partial u/\partial r$ vanishes very quickly as r increases, so that the integrand in the above integral goes to 0 long before we hit the boundary of the box. Given that, extending the integral out to ∞ just adds a lot of zero to the integral, which will not change the answer!

Integrating over the angles, we obtain

$$\frac{\partial I}{\partial V} = -\frac{4\pi\beta}{3V^2}\int_0^{\infty} dr\, r^3 \frac{du}{dr}e^{-\beta u(r)} \tag{1.4.39}$$

We now simplify this expression by the integral as

$$\frac{\partial I}{\partial V} = \frac{4\pi\beta}{3V^2}\frac{1}{\beta}\int_0^\infty dr\, r^3 \frac{d}{dr} e^{-\beta u(r)} \tag{1.4.40}$$

which we can integrate by parts to give

$$\frac{\partial I}{\partial V} = \frac{4\pi}{3V^2}\left[r^3\, e^{-\beta u(r)}\Big|_0^\infty - \int_0^\infty dr \left(\frac{d}{dr} r^3\right) e^{-\beta u(r)}\right] \tag{1.4.41}$$

Unfortunately, when we try to evaluate the first term, we find that it is ∞ at $r = \infty$. Even if we admit that this is a consequence of our approximation that r can be integrated out to ∞, it does not really matter because this term would simply increase with increasing system size, i.e., increasing volume, which is unphysical, as the pressure cannot behave this way – pressure is an *intensive* quantity. Fortunately, there is a trick that can save us. Recognizing that $u(r) \to 0$ as $r \to \infty$, $exp(-\beta u(r)) \to 1$ as $r \to \infty$. Hence, let us back up and just subtract this one from the exponential where we introduce the derivative. That is, if we write

$$\frac{\partial I}{\partial V} = \frac{4\pi\beta}{3V^2}\frac{1}{\beta}\int_0^\infty dr\, r^3 \frac{d}{dr} e^{-\beta u(r)} = \frac{4\pi\beta}{3V^2}\frac{1}{\beta}\int_0^\infty dr\, r^3 \frac{d}{dr}(e^{-\beta u(r)} - 1) \tag{1.4.42}$$

we do not change anything since the derivative of 1 with respect to r is 0 anyway. We can now integrate this by parts to give

$$\frac{\partial I}{\partial V} = \frac{4\pi}{3V^2}\left[r^3\left(e^{-\beta u(r)} - 1\right)\Big|_0^\infty - \int_0^\infty dr \left(\frac{d}{dr} r^3\right)\left(e^{-\beta u(r)} - 1\right)\right] \tag{1.4.43}$$

Now the first term vanishes both at $r = 0$ and at $r = \infty$, and we are left with

$$\frac{\partial I}{\partial V} = -\frac{4\pi}{V^2}\int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right) \tag{1.4.44}$$

and the pressure becomes

$$P = \frac{N k_B T}{V} - \frac{N^2 k_B T}{V^2}\, 2\pi \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right) \tag{1.4.45}$$

Using the fact that $R = N_0 k_B$, and introducing the density $\rho = n/V$, we finally obtain

$$P = \rho RT + \rho^2 RT\left[-2\pi N_0 \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right)\right] \tag{1.4.46}$$

$$\frac{P}{\rho RT} = 1 + \rho\left[-2\pi N_0 \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right)\right] \tag{1.4.47}$$

The term in brackets is denoted $B_2(T)$:

$$B_2(T) = -2\pi N_0 \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right) \tag{1.4.48}$$

and is called a *virial coefficient*, as it arises from the classical mechanical virial mentioned above.

More realistic treatments of non-ideal gases generate an equation of state in the form of a power series in the density in which all of the coefficients are functions of temperature. This can be expressed as

$$\frac{P}{\rho RT} = 1 + \sum_{k=1}^{\infty} B_{k+1}(T)\rho^k \tag{1.4.49}$$

This equation of state is called the *virial equation of state*. The coefficients $B_{k+1}(T)$are called *virial coefficients*. In the low density limit, the most important term in this power series is the $k = 1$ or linear term, which gives the approximate equation of state

$$\frac{P}{\rho RT} \approx 1 + B_2(T)\rho \tag{1.4.50}$$

where the dominant coefficient $B_2(T)$ is called the *second virial coefficient*. These can be measured experimentally. The following plot shows the second virial coefficient for several gases. Although it is difficult to see, these curves pass

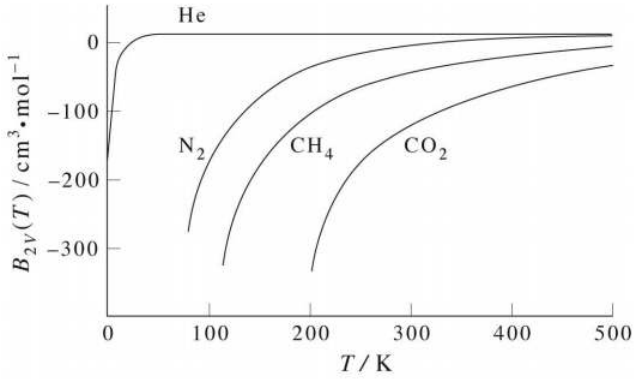


Figure 4.2: Experimental second virial coefficient plots for several real gases.

through a shallow maximum that is not captured by the van der Waals equation. Thus, the van der Waals equation is only in qualitative agreement with these but is not fully quantitative.

Let us look at some simple examples of $B_2(T)$ calculations.

1. **Hard-sphere potential**:

$$u(r) = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases} \tag{1.4.51}$$

For this potential, the calculation of $B_2(T)$ proceeds as follows:

$$B_2(T) = -2\pi N_0 \left[\int_0^\sigma \left(e^{-\beta\cdot\infty} - 1\right) r^2 dr + \int_\sigma^\infty \left(e^{-\beta\cdot 0} - 1\right) r^2 dr \right] \tag{1.4.52}$$

$$= -2\pi N_0 \left[\int_0^\sigma (0-1)\, r^2 dr + \int_\sigma^\infty (1-1)\, r^2 dr \right] \tag{1.4.53}$$

$$= 2\pi N_0 \int_0^\sigma r^2 dr \tag{1.4.54}$$

$$= \frac{2}{3}\pi\sigma^3 N_0 \tag{1.4.55}$$

which is also the parameter b in the van der Waals equation. In this case, there is no temperature dependence in the result for $B_2(T)$.

2. **Square-well potential plus hard-sphere potential**: In this case, the potential takes the form

$$u(r) = \begin{cases} \infty & r \le \sigma \\ -\epsilon & \sigma \le r \le \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} \tag{1.4.56}$$

In this case, the hard-sphere potential is supplemented by a short-range constant attractive potential that has a “square-well” shape. The parameter $\lambda > 1$ determines the range of the square well. For this example, the calculation of $B_2(T)$ proceeds as follows:

$$B_2(T) = -2\pi N_0 \left[\int_0^{\sigma} \left(e^{-\beta\cdot\infty} - 1\right) r^2 dr + \int_{\sigma}^{\lambda\sigma} \left(e^{\beta\epsilon} - 1\right) r^2 dr + \int_{\lambda\sigma}^{\infty} \left(e^{-\beta\cdot 0} - 1\right) r^2 dr \right] \tag{1.4.57}$$

$$= -2\pi N_0 \left[-\int_0^{\sigma} r^2 dr + \left(e^{\beta\epsilon} - 1\right) \int_{\lambda\sigma}^{\infty} r^2 dr \right] \tag{1.4.58}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \left(e^{\beta\epsilon} - 1\right) \frac{r^3}{3} \Big|_{\sigma}^{\lambda\sigma} \right] \tag{1.4.59}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \left(e^{\beta\epsilon} - 1\right) \frac{1}{3} \left(\lambda^3\sigma^3 - \sigma^3\right) \right] \tag{1.4.60}$$

$$= \frac{2\pi N_0 \sigma^3}{3} \left[1 - \left(e^{\beta\epsilon} - 1\right) \left(\lambda^3 - 1\right) \right] \tag{1.4.61}$$

A plot of this second virial coefficient is given in the figure below.

3. **Hard-sphere plus $-C_6/r^6$ potential**: For this example, the potential is

$$u(r) = \begin{cases} \infty & r \le \sigma \\ -\frac{C_6}{r^6} & r > \sigma \end{cases} \tag{1.4.62}$$

This is a particular realization of a potential that leads to the van der Waals equation of state. The $-C_6/r^6$ attractive part of the potential comes directly from a full quantum mechanical treatment of the electron distribution around each atom in an interacting pair. Such an attractive potential attempts to model London dispersion or van der Waals forces. For this example, the calculation of $B_2(T)$ proceeds as follows:

$$B_2(T) = -2\pi N_0 \left[\int_0^{\sigma} \left(e^{-\beta\cdot\infty} - 1\right) r^2 dr + \int_{\sigma}^{\infty} \left(e^{\beta C_6/r^6} - 1\right) r^2 dr \right] \tag{1.4.63}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \int_{\sigma}^{\infty} \left(e^{\beta C_6/r^6} - 1\right) r^2 dr \right] \tag{1.4.64}$$

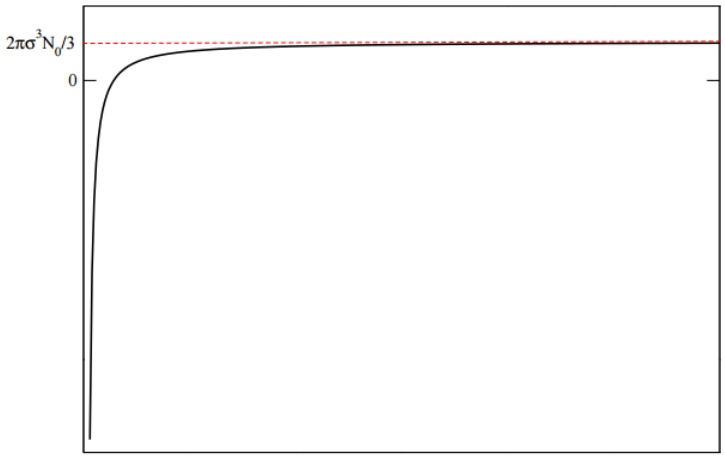


Figure 4.3: Second virial coefficient for the hard-sphere plus square-well potential.

The remaining integral cannot be evaluated in closed form, but let us suppose that $\beta C_6/r^6 \ll 1$ for all values of r considered, i.e., $\sigma \le r < \infty$. Then, we can expand the exponential using the power series $e^x \approx 1 + x + x^2/2! + \cdots$. If we retain just the first two terms, then we have the approximation

$$e^{\beta C_6/r^6} - 1 \approx 1 + \frac{\beta C_6}{r^6} - 1 = \frac{\beta C_6}{r^6} \tag{1.4.65}$$

With this approximation, the calculation of $B_2(T)$ can proceed as follows:

$$B_2(T) \approx -2\pi N_0 \left[-\frac{\sigma^3}{3} + \beta C_6 \int_\sigma^\infty \frac{1}{r^6} r^2 dr \right] \tag{1.4.66}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \beta C_6 \int_\sigma^\infty \frac{1}{r^4} dr \right] \tag{1.4.67}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \beta C_6 \left(-\frac{1}{3r^3} \Big|_\sigma^\infty \right) \right] \tag{1.4.68}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \frac{\beta C_6}{3\sigma^3} \right] \tag{1.4.69}$$

$$= \frac{2\pi N_0 \sigma^3}{3} \left[1 - \frac{C_6}{3k_B T \sigma^6} \right] \tag{1.4.70}$$

A plot of this function will follow the curve presented in the figure below.

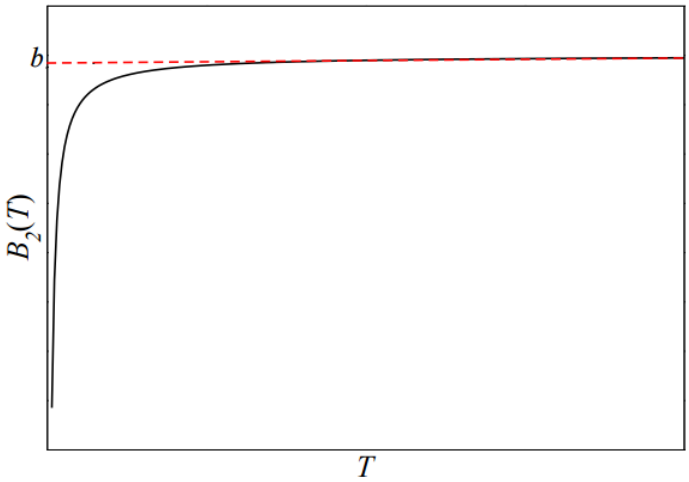


Figure 4.4: Second virial coefficient for the hard-sphere plus $-C_6/r^6$ *potential.*

However, in this example, we can improve the approximation by retaining more terms of the exponential we expanded above. In fact, let us see what happens if we retain *all* of the terms in the power series. That is, we will use the fact that e^x can be represented exactly as

$$e^x = \sum_{k=0}^{\infty} \frac{x^k}{k!} = 1 + \sum_{k=1}^{\infty} \frac{x^k}{k!} \tag{1.4.71}$$

so that

$$e^{\beta C_6/r^6} - 1 = \sum_{k=1}^{\infty} \frac{1}{k!} \left(\frac{\beta C_6}{r^6} \right)^k \tag{1.4.72}$$

$$= 1 + \sum_{k=1}^{\infty} \frac{\beta^k C_6^k}{k!} \frac{1}{r^{6k}} \tag{1.4.73}$$

With the expansion, the calculation of $B_2(T)$ proceeds as follows:

$$B_2(T) = -2\pi N_0 \left[-\frac{\sigma^3}{3} + \sum_{k=1}^{\infty} \frac{\beta^k C_6^k}{k!} \int_\sigma^\infty \frac{1}{r^{6k}} r^2 dr \right] \tag{1.4.74}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \sum_{k=1}^{\infty} \frac{\beta^k C_6^k}{k!} \int_\sigma^\infty \frac{1}{r^{6k-2}} dr \right] \tag{1.4.75}$$

$$= -2\pi N_0 \left[-\frac{\sigma^3}{3} + \sum_{k=1}^{\infty} \frac{\beta^k C_6^k}{k!} \frac{1}{(6k-1)\,\sigma^{6k-1}} \right] \tag{1.4.76}$$

$$= \frac{2\pi N_0 \sigma^3}{3} \left[1 - 3 \sum_{k=1}^{\infty} \frac{(\beta C_6)^k}{k!} \frac{1}{(6k-1)\,\sigma^{6k+2}} \right] \tag{1.4.77}$$

The final result represents an exact expression for $B_2(T)$ for this particular model of $u(r)$. How does it improve on the result obtained above retaining just two terms in the expansion of the exponential? Let us plot the final result as a function of temperature in the following way: Unfortunately, we cannot resum the final expression into a nice closed form, but we can evaluate the sum numerically on a computer. However, on a computer, we cannot sum an *infinite* number of terms. Rather, we replace the upper limit of ∞ with a maximum number of terms $K_{\max}$ and then just increase $K_{\max}$ until the result converges. So, let's do that for several values of $K_{\max}$ and see how the curve changes as we increase $K_{\max}$. This will show us how the result converges with $K_{\max}$. The result is shown in the figure below. We see from the figure that the sum converges very rapidly with $K_{\max}$

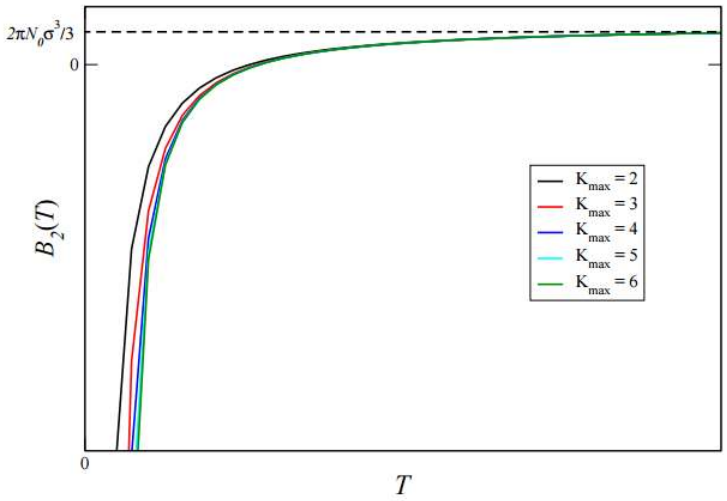


Figure 4.5: Second virial coefficient for the potential in Equation 4.47.

and only requires a few terms. Not unexpectedly, the most significant deviations from $K_{\max} = 2$ occur in the low-temperature part of the curves.

4. Perhaps the most realistic representation of the potential $u(r)$ shown in Figure 2.2 is the so-called Lennard-Jones potential, for which

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1.4.78}$$

A plot of this potential very closely resembles that shown in Figure 2.2. In particular, there is a well-defined minimum, which we can compute by taking the derivative of $u(r)$, setting it to 0, and solving for r at that point:

$$U'(r) = -4\epsilon\left[\frac{12\sigma^{12}}{r^{13}} - \frac{6\sigma^6}{r^7}\right] = 0 \tag{1.4.79}$$

$$\frac{12\sigma^{12}}{r^{13}} = \frac{6\sigma^6}{r^7} \tag{1.4.80}$$

$$\frac{2\sigma^6}{r^{13}} = \frac{1}{r^7} \tag{1.4.81}$$

$$2\sigma^6 = r^6 \tag{1.4.82}$$

$$r = 2^{1/6}\sigma \equiv r_m \tag{1.4.83}$$

where r_m denotes the location of the minimum. The value of the Lennard-Jones potential at that point is

$$u(r_m) = u\left(2^{1/6}\sigma\right) = 4\epsilon\left[\left(\frac{\sigma}{2^{1/6}\sigma}\right)^{12}\left(\frac{\sigma}{2^{1/6}\sigma}\right)^{6}\right] \tag{1.4.84}$$

$$= 4\epsilon\left[\frac{1}{2^2} - \frac{1}{2}\right] \tag{1.4.85}$$

$$= -4\epsilon \cdot \frac{1}{4} \tag{1.4.86}$$

$$= -\epsilon \tag{1.4.87}$$

Thus, the parameter ϵ measures the depth of the minimum at $r = r_m$. In addition, $u(\sigma)$, and for $r < \sigma$, the potential exhibits a very steep increase, very much like the hard-sphere potential. Hence, σ is a measure of the van der Waals radius of each particle.

The calculation of the second virial coefficient can now be set up as

$$B_2(T) = -2\pi N_0 \int_0^\infty \left\{ exp\left(-4\beta\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] - 1 \right) \right\} r^2 dr \tag{1.4.88}$$

Let us make a change of variables from r to

$$x = \frac{r}{\sigma}$$

so that $dr = \sigma dx$. Let us also define $\beta^* = \beta\epsilon$. With this change, the integral for $B_2(T)$ becomes

$$B_2(T) = -2\pi\sigma^3 N_0 \int_0^\infty \left[e^{-4\beta^*(x^{-12} - x^{-6})} - 1 \right] x^2 dx \tag{1.4.89}$$

Again, this integral cannot be evaluated analytically in closed form. We could expand the exponential in an infinite series as we did in the previous example. However, if we were to do this, the evaluation of the various terms in the integral would be considerably more complicated than in the previous example, as we would need to evaluated increasingly higher powers of a binomial form $(x^{-12} - x^{-6})^k$. Instead, since this is just a one-dimensional integral, we can evaluate it numerically using a method such as Simpson's rule. Recall that Simpson's rule for the integral of a function $f(x)$ using a set of n evenly spaced values for x $(x_0, x_1, \ldots, x_n)$ is just

$$\int_a^b f(x)dx \approx \frac{h}{3} \tag{1.4.90}$$
$$[f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + 2f(x_4) + \cdots + 2f(x_{n-2}) + 4f(x_{n-1}) + f(x_n)]$$

where $h = (b-a)/n$, and the points $x_0, \ldots, x_n$ are given by $x_j = a + jh, j = 0, \ldots, n$.

Applying this to the integral in Equation 4.58, the resulting curve for $B_2(T)$ as a function of T appears as in the figure below: In this figure, $k_B T^* = 1/\beta^*$, and

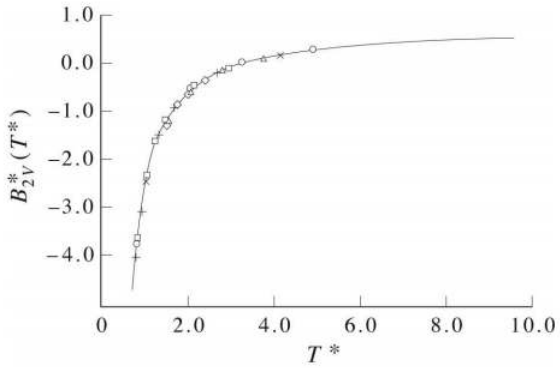


Figure 4.6: Second virial coefficient for the Lennard-Jones potential evaluated using numerical integration. Experimental points are also plotted. Because of the use of "reduced" units, data for all gases land on a single master curve, as an example of the law of corresponding states.

$$B_2^*(T) = \frac{B_2(T)}{2\pi\sigma^3 N_0/3}$$

Unfortunately, the curve in the book does not carry the curve out to high enough temperature to see the maximum. However, on page 233 of the book *Statistical Mechanics* by Donald A. McQuarrie, a more complete curve for the Lennard-Jones potential is shown, and in this curve the temperature axis is sufficiently long to see the maximum. This book is available on Google Books.

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1.5: The van der Waals equation of state and radial distribution functions

The Van der Waals Equation of State

In the last lecture, we saw that for the pair potential

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\dfrac{C_6}{r^6} & r > \sigma \end{cases} \tag{1.5.1}$$

we could write the second virial coefficient as

$$B_2(T) = \frac{2}{3}\pi N_0 \sigma^3 \left[1 - \frac{C_6}{3k_B T \sigma^6}\right] \tag{1.5.2}$$

Let us introduce to simplifying variables

$$b = \frac{2}{3}\pi N_0 \sigma^3 \tag{1.5.3}$$

$$a = \frac{2\pi N_0^2 C_6}{9\sigma^3} \tag{1.5.4}$$

in terms of which

$$B_2(T) = b - \frac{a}{RT} \tag{1.5.5}$$

With these definitions, the virial equation of state becomes

$$P = \frac{nRT}{V} + \frac{n^2}{V^2} RT \left(b - \frac{a}{RT}\right) \tag{1.5.6}$$

$$= \frac{nRT}{V}\left(1 + \frac{nb}{V}\right) - \frac{an^2}{V^2} \tag{1.5.7}$$

If we assume nb/V is small, then we can also write

$$1 + \frac{nb}{V} \approx \frac{1}{1 - \dfrac{nb}{V}} \tag{1.5.8}$$

so that

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{1.5.9}$$

which is known as the *van der Waals* equation of state.

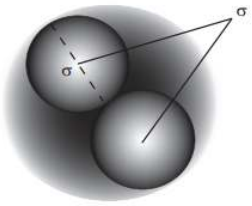


Figure 1.5.1: Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

The first term in this equation is easy to motivate. In fact, it looks very much like the equation of state for an ideal gas having volume $V - nb$ rather than V. This part of the van der Waals equation is due entirely to the hard-wall potential $u_o(r)$. Essentially, this potential energy term describes a system of "billiard balls" of diameter σ. The figure below shows two of these billiard ball type particles at the point of contact (also called the distance of closest approach). At this point, they undergo a collision and separate, so that cannot be closer than the distance shown in the figure. At this point, the distance between their centers is also σ, as the figure indicates. Because of this distance of closest approach, the total volume available to the particles is not V but some

volume less than V. This reduction in volume can be calculated as follows: Figure 1.5.1 shows a shaded sphere that just contains the pair of billiard ball particles. The volume of this sphere is the volume excluded from any two particles. The radius of the sphere is σ as the figure shows. Hence, the excluded volume for the two particles is $4\pi\sigma^3/3$, which is the volume of the shaded sphere. From this, we see that the excluded volume for any *one* particle is just half of this or $2\pi\sigma^3/3$. The excluded volume for a mole of such particles is just $2\pi\sigma^3 N_0/3$, which is the parameter b:

$$b = \frac{2}{3}\pi\sigma^3 N_0 \tag{1.5.10}$$

Given n moles of gas, the total excluded volume is then nb, so that the total *available* volume is simply $V - nb$.

Isotherms of the van der Waals equation are shown in the figure below (left panel). In the figure the volume axis is the molar volume denoted $\bar{V} = V/n$. At sufficiently high temperature, the isotherms approach those of an ideal gas. However, we also see something strange in some of the isotherms. Specifically, we see a region in which P and V increase together, and we know that this cannot actually happen in a real gas. It should be clear that many approximations and assumptions go into the derivation of the van der Waals equation so that some of the important physics is missing from the model. Hence, we should not be surprised if the van der Waals equation has some unphysical behavior buried in it.

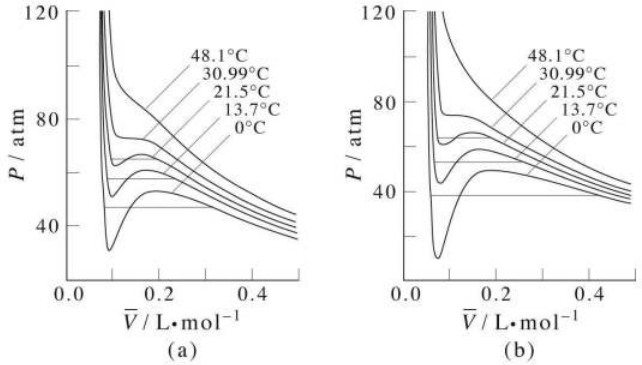


Figure 1.5.2: Isotherms of the van der Waals equation of state using parameters a and b computed for carbon dioxide.

In fact, we know that at sufficiently low temperatures, any real gas, when compressed, must undergo a transition from gas to liquid. The signature of such a transition is a discontinuous change in the volume, signifying the condensation of the gas into a liquid that occupies a significantly lower volume. Unfortunately, the van der Waals equation does not correctly predict this behavior, and hence, it must be added in *ad hoc*. This is done by drawing a horizontal line through the isotherm (Figure 1.5.2) and in the figure below. The vertical position of the line is

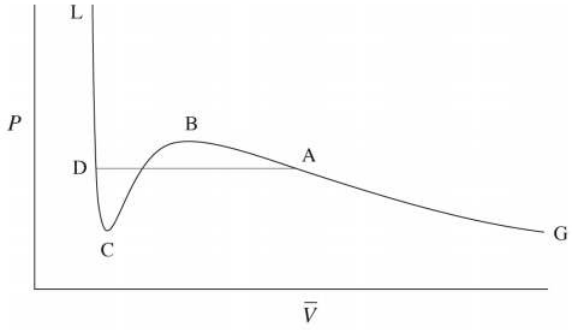


Figure 1.5.3: Illustration of the tie line in the van der Waals equation.

chosen so that the area above the line (between the line and the isotherm) and below the line (again between the line and the isotherm) is exactly the same. In this way, we entirely remove the artifact of the unphysical increase of P with V when we compute the compressional work on the gas from $\int P(V)\,dV$, to be discussed in our section on thermodynamics. This horizontal line is called the *tie line*.

As it happens, there is exactly one isotherm along which the van der Waals equation correctly predicts the gas-to-liquid phase transition. Along this isotherm, the volume discontinuity captured by the tie line is shrunken down to a single point (so that there is

no possibility of an increase of P with V!). This isotherm, in fact, corresponds to the highest possible temperature at which such a transition can occur. As we approach this isotherm from higher temperatures, this isotherm is a kind of dividing line between the system's remaining a gas at all value of P and V and the system's actually undergoing a gas-to-liquid transition. Hence, this isotherm is called the *critical isotherm* (Figure 1.5.4): The temperature of this isotherm is called the critical temperature, denoted T_c. The point at which the curve flattens out, signifying the phase transition, is called the *critical point*. If we draw a curve through the isotherms joining all points of these isotherms at which the tie lines begin, continue the curve up to the critical isotherm, and down the other side where the tie lines end, this curve reaches a maximum at the critical point. This is illustrated below:

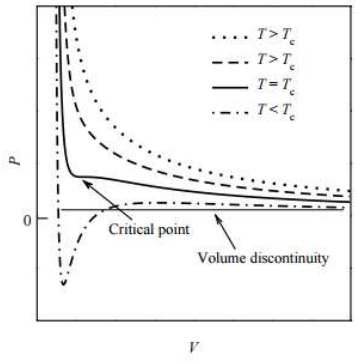


Figure 1.5.4: Isotherms of the van der Waals equation of state for four different temperatures with explicit illustration of the critical isotherm.

The shape of the critical isotherm at the critical point allows us to determine the exact temperature, pressure, and volume at which the phase transition from gas to liquid will occur. At this point, the isotherm is both horizontal and flat. This means that both the first and second derivatives of P with respect to V must vanish:

$$\frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0 \tag{1.5.11}$$

Substituting the van der Waals equation into these two conditions, we find the following:

$$-\frac{nRT}{(V-nb)^2} + \frac{2an^2}{V^3} = 0 \tag{1.5.12}$$

$$\frac{2nRT}{(V-nb)^3} - \frac{6an^2}{V^4} = 0 \tag{1.5.13}$$

Hence, we have two equations in two unknowns V and T for the critical temperature and critical volume. Once these are determined, the van der Waals equation, itself, allows us to determine the critical pressure.

To solve the equations, first divide one by the other. This gives us a simple condition for the volume:

$$\frac{V-nb}{2} = \frac{V}{3} \tag{1.5.14}$$

$$3V - 3nb = 2V \tag{1.5.15}$$

$$V = 3nb \equiv V_c \tag{1.5.16}$$

This is the critical volume. Now use either of the two conditions to obtain the critical temperature T_c. If we use the first one, we find

$$\frac{nRT_c}{(V_c-nb)^2} = \frac{2an^2}{V_c^3} \tag{1.5.17}$$

$$\frac{nRT_c}{(3nb-nb)^2} = \frac{2an^2}{(3nb)^3} \tag{1.5.18}$$

$$\frac{nRT_c}{4n^2b^2} = \frac{2an^2}{27n^3b^3} \tag{1.5.19}$$

$$RT_c = \frac{8a}{27b} \tag{1.5.20}$$

Finally, plugging the critical temperature and volume into the van der Waals equation, we obtain the critical pressure

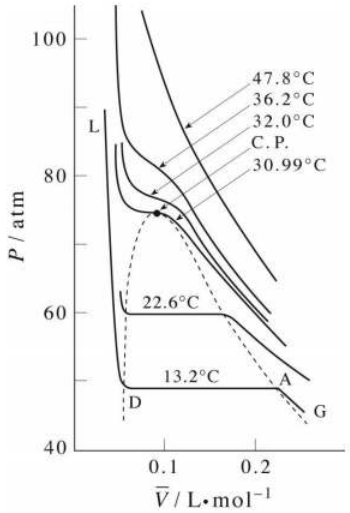


Figure 1.5.5: Illustration of the curve (dashed line) joining the beginning and ends of the tie lines. This curve reaches a maximum at the critical point.

as

$$P = \frac{nRT_c}{V_c - nb} - \frac{an^2}{V_c^2} \tag{1.5.21}$$

$$= \frac{8an/27b}{3nb - nb} - \frac{an^2}{(3nb)^2} \tag{1.5.22}$$

$$= \frac{a}{27b^2} \tag{1.5.23}$$

Structure of Liquids

Characterizing the structure and thermodynamics of liquids is obviously more challenging than it is for gases because the types of approximations that work for gases do not for liquids, and we need to take into account the full set of interactions in constructing the partition function. Although there are analytical theories that have been developed for liquids (such as integral-equation theory, one of the developers of which is our Jerome Percus at the Courant Institute), these theories have largely been supplanted by computer simulations, which yield more accurate results and can be applied to liquids of essentially any complexity.

In terms of statistical mechanics, one of the most important quantities used to characterize the nature of the liquid 6 state is the co-called *radial distribution function* or *pair correlation function*. It is denoted $g(r)$ and is defined to be

$$g(r) = \frac{(N-1)}{4\pi\rho r^2}\frac{1}{Z}\int_{|\mathbf{r}_1-\mathbf{r}_2|=r} d\mathbf{x}_\mathbf{r}\, e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{1.5.24}$$

where

$$Z = \int d\mathbf{x}_\mathbf{r}\, e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{1.5.25}$$

is the configurational partition function. Physically, the quantity $r^2 g(r)\, dr$ gives us the fraction of particles or the probability that a particle is in a spherical shell of thickness dr at a distance r from another particle. Because of attractive forces between particles in liquids, each particle in a liquid tends to be surrounded by a "shell" of other particles at some average distance. This shell is called a *solvation shell* or *coordination shell* or, when the liquid is water, a *hydration shell*. Particles in this solvation shell also have their own solvation shells, and these have solvation shells, and so forth. Thus, a liquid can actually exhibit a surprising amount of structure, and the function $g(r)$ captures that structure very clearly. Moreover, $g(r)$ is a function that can be measured experimentally using the techniques of neutron or X-ray scattering in a setup that is somewhat analogous to Bragg scattering from crystals. Recall that Bragg scattering is used to measure the distance between crystalline planes in a solid. In a liquid, the particles are in constant motion, so there are no well-defined distances, however, certain average distance values are favored over others, and these scattering experiments capture these average distances just as Bragg scattering experiments capture more fixed distances in solids.

Figure 1.5.6 shows the radial distribution functions for liquid argon at several different temperatures. Not only can we see

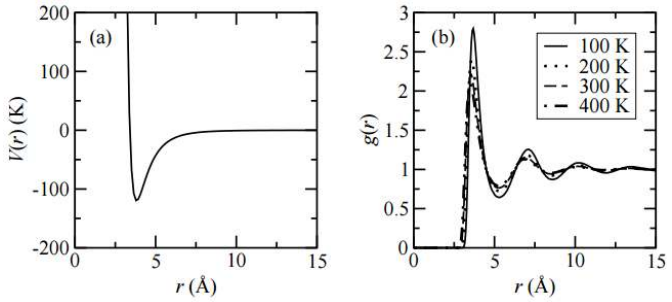


Figure 1.5.6: Radial distribution functions for liquid argon at several temperatures.

the existence of several solvation shells, we can read off the plot the distances at which these solvation shells peak around a central atom in the liquid. From the plot, we clearly see that $g(r)$ is a function of temperature and depends sensitively on it. In particular, as temperature increases, structure tends to decrease.

In the same way, Figure 1.5.7 shows that the radial distribution function also depends on pressure. We see the same liquid argon system subject to several pressures. Even though the volume fluctuations (see panel on the left) tend to be small, pressure changes somewhat the degree of structuring in the liquid. In particular, as we compress the liquid, it tends to become more structured, as we might expect. At higher pressures, particles are less likely to escape from solvation shells and tend to fluctuate less within these solvation shells.

Finally, we show the three radial distribution functions of water, including computer simulation results and the experimental results from neutron scattering and X-ray scattering. In the case of the computer simulations, the

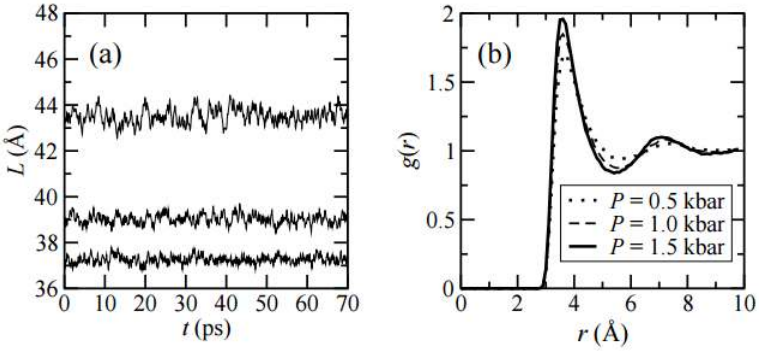


Figure 1.5.7: Radial distribution functions for liquid argon at several pressures.

calculations are performed using a technique known as *ab initio* or first-principles molecular dynamics. In this approach, the forces and potential energies for each nuclear configuration are generated by direct solution of the Schrödinger equation (based on the approximation of density functional theory). This allows to generate these functions with absolutely no experimental input parameters – they really do come from first principles.

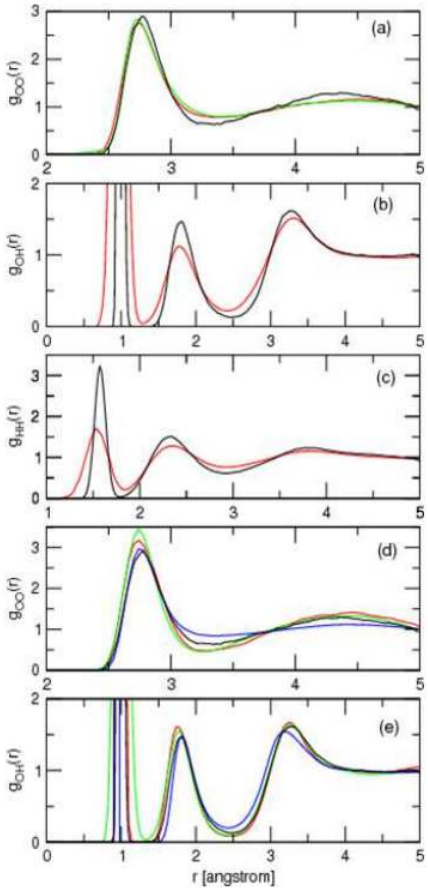


Figure **1.5.8**: Oxygen-oxygen, Oxygen-hydrogen and Hydrogen-hydrogen radial distribution functions for water a STP. Experiment comes from the neutron scattering results of Soper et al. (red) and X-ray results are from the group of T. Head-Gordon (green). The computer simulation results are from the work of Lee and Tuckerman (black).

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1.6: Equipartitioning, Collisions, and Random Walks

Equipartitioning of Energy

When the mechanical energy is

$$\mathcal{E}(x) = \mathcal{H}(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{1.6.1}$$

the canonical distribution function nicely separates into a product of momentum and coordinate distributions:

$$f(x) = \frac{C_N}{Q(N,V,T)} \left[e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2/2m_i} \right] \left[e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \right] \tag{1.6.2}$$

$$= \frac{C_N}{Q(N,V,T)} \left[\prod_{i=1}^{N} e^{-\beta \mathbf{p}_i^2/2m_i} \right] \left[e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \right] \tag{1.6.3}$$

$$= \left[\prod_{i=1}^{N} P(\mathbf{p}_i) \right] \left[\frac{1}{Z} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \right] \tag{1.6.4}$$

$$= \left[\prod_{i=1}^{N} \mathcal{P}(p_{x,i})\ \mathcal{P}(p_{y,i})\ \mathcal{P}(p_{z,i}) \right] \left[\frac{1}{Z} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \right] \tag{1.6.5}$$

where $P(\mathbf{p}_i)$ is the Maxwell-Boltzmann distribution as a function of the momentum $\mathbf{p}_i$.

Given this decomposition of the momentum distribution into products of distributions of individual components, we always have, for any system,

$$\left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} N k_B T \tag{1.6.6}$$

However, in addition to this, we also have the following averages:

$$\left\langle \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} k_B T \tag{1.6.7}$$

and

$$\left\langle \frac{p_{x,i}^2}{2m_i} \right\rangle = \frac{1}{2} k_B T, \quad \left\langle \frac{p_{y,i}^2}{2m_i} \right\rangle = \frac{1}{2} k_B T, \quad \left\langle \frac{p_{z,i}^2}{2m_i} \right\rangle = \frac{1}{2} k_B T \tag{1.6.8}$$

The fact that these averages can be written for every individual component tells us that each degree of freedom has an average of $k_B T/2$ energy associated with it. This is called *equipartitioning of energy*.

How does equipartitioning happen? It occurs through the interactions in the system, which dynamically, produce collisions, leading to covalent bond breaking and forming events, hydrogen bond breaking and forming events, halogen bond breaking and forming events, diffusion, and so forth, all depending on the chemical composition of the system. Each individual collision event leads to a transfer of energy from one particle to another, so that, on average, all particles have the same energy $k_B T/2$. This does not mean that, at any instant, this is the energy of a randomly chosen particle. Obviously, there are considerable fluctuations in the energy of any one particle, however, the average over these fluctuations must produce the value $k_B T/2$.

A system obeys a well defined set of classical equations of motion, so that we can, in principle, determine exactly when the next collision will occur and exactly how much energy will be transferred in the collision. However, since we do not follow the detailed motion of all of the particles, our description of collisions and their consequences must be statistical in nature. We begin by defining a few simple terms that are commonly used for this subject.

Collision energy

Consider two particles A and B in a system. The kinetic energy of these two particles is

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} \tag{1.6.9}$$

Let us change to center-of-mass $(\mathbf{P})$ and relative $(\mathbf{p})$ momenta, which are given by

$$\mathbf{P} = \mathbf{p}_A + \mathbf{p}_B, \quad \mathbf{p} = \frac{m_B \mathbf{p}_a - m_A \mathbf{p}_B}{M} \tag{1.6.10}$$

where $M = m_A + m_B$ is the total mass of the two particles. Substituting this into the kinetic energy, we find

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} \tag{1.6.11}$$

where

$$\mu = \frac{m_A m_B}{M} \tag{1.6.12}$$

is called the *reduced mass* of the two particles. Note that the kinetic energy separates into a sum of a center-of-mass term and a relative term.

Now the relative position is $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$ so that the relative velocity is $\dot{\mathbf{r}} = \dot{\mathbf{r}}_A - \dot{\mathbf{r}}_B$ or $\mathbf{v} = \mathbf{v}_A - \mathbf{v}_B$. Thus, if the two particles are approaching each other such that $\mathbf{v}_A = -\mathbf{v}_B$, then $\mathbf{v} = 2\mathbf{v}_A$. However, by equipartitioning the relative kinetic energy, being mass independent, is

$$\left\langle \frac{\mathbf{p}^2}{2\mu} \right\rangle = \frac{3}{2} k_B T \tag{1.6.13}$$

which is called the *collision energy*

Collision cross section

Consider two molecules in a system. The probability that they will collide increases with the effective "size" of each particle. However, the size measure that is relevant is the apparent cross-section area of each particle. For simplicity, suppose the particles are spherical, which is not a bad approximation for small molecules. If we are looking at a sphere, what we perceive as the size of the sphere is the cross section area of a great circle. Recall that each spherical particle has an associated "collision sphere" that just encloses two particles at closest contact, i.e., at the moment of a collision, and that this sphere is a radius d, where d is the diameter of each spherical particle (see lecture 5). The cross-section of this collision sphere represents an effective cross section for each particle inside which a collision is imminent. The cross-section of the collision sphere is the area of a great circle, which is πd^2. We denote this apparent cross section area σ. Thus, for spherical particles A and B with diameters d_A and d_B, the individual cross sections are

$$\sigma_A = \pi d_A^2, \quad \sigma_B = \pi d_B^2 \tag{1.6.14}$$

The *collision cross section*, σ_{AB} is determined by an effective diameter d_{AB} characteristic of both particles. The collision probability increases of both particles have large diameters and decreases if one of them has a smaller diameter than the other. Hence, a simple measure sensitive to this is the arithmetic average

$$d_{AB} = \frac{1}{2}(d_A + d_B) \tag{1.6.15}$$

and the resulting collision cross section becomes

$$\begin{aligned}
\sigma_{AB} &= \pi d_{AB}^2 && (1.6.16)\\
&= \pi \left(\frac{d_A + d_B}{2} \right)^2 && (1.6.17)\\
&= \frac{\pi}{4}(d_A^2 + 2d_A d_B + d_B^2) && (1.6.18)\\
&= \frac{1}{4}(\sigma_A + 2\sqrt{\sigma_A \sigma_B} + \sigma_B) && (1.6.19)\\
&= \frac{1}{2}\left[\left(\frac{\sigma_A + \sigma_B}{2} \right) + \sqrt{\sigma_A \sigma_B} \right] && (1.6.20)
\end{aligned}$$

which, interestingly, is an average of the two types of averages of the two individual cross sections, the arithmetic and geometric averages!

Average collision Frequency

Consider a system of particles with individual cross sections σ. A particle of cross section σ that moves a distance l in a time Δt will sweep out a cylindrical volume (ignoring the spherical caps) of volume σl (Figure 1.6.1). If the system has a number density ρ, then the number of collisions that will occur is

$$N_{\text{coll}} = \rho\sigma l \tag{1.6.21}$$

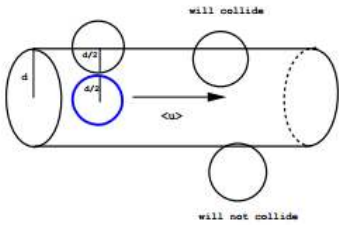


Figure 1.6.1: Collision cylinder. Any particle that partially overlaps with this volume will experience a collision with a test particle tracing out this volume.

We define the average collision rate as $N_{\text{coll}}/\Delta t$, i.e.,

$$\gamma = \frac{N_{\text{coll}}}{\Delta t} = \frac{\rho\sigma l}{\Delta t} = \rho\sigma\langle|\mathbf{v}|\rangle \tag{1.6.22}$$

where $\langle|\mathbf{v}|\rangle$ is the average relative speed. If all of the particles are of the same type (say, type A), then performing the average over a Maxwell-Boltzmann speed distribution gives

$$\langle|\mathbf{v}|\rangle = \sqrt{\frac{8k_BT}{\pi\mu}} \tag{1.6.23}$$

where $\mu = m_A/2$ is the reduced mass. The average speed of a particle is

$$\langle|\mathbf{v}_A|\rangle = \sqrt{\frac{8k_BT}{\pi m_A}} \tag{1.6.24}$$

so that

$$\langle|\mathbf{v}|\rangle = \sqrt{2}\langle|\mathbf{v}_A|\rangle \tag{1.6.25}$$

Mean Free Path

The mean free path is defined as the distance a particle will travel, on average, before experiencing a collision event. This is defined as the product of the speed of a particle and the time between collisions. The former is $\langle|\mathbf{v}|\rangle/\sqrt{2}$, while the latter is $1/\gamma$. Hence, we have

$$\lambda = \frac{\langle|\mathbf{v}|\rangle}{\sqrt{2}\rho\sigma\langle|\mathbf{v}|\rangle} = \frac{1}{\sqrt{2}\rho\sigma} \tag{1.6.26}$$

Random Walks

In any system, a particle undergoing frequent collisions will have the direction of its motion changed with each collision and will trace out a path that appears to be random. In fact, if we treat the process as statistical, then, we are, in fact, treating each collision event as a random event, and the particle will change its direction at random times in random ways! Such a path might appear as shown in Figure \(\PageIndex{2. Such a path is often referred to as a *random walk path*.

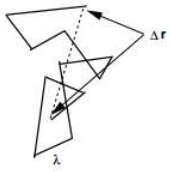


Figure **1.6.2**: Random walk path.

In order to analyze such paths, let us consider a random walk in one dimension. We'll assume that the particle move a mean-free path length λ between collisions and that each collision changes the direction of the particles motion, which in one dimension, means that the particle moves either to the right or to the left after each event. This can be mapped onto a metaphoric "coin toss" that can come up heads "H" or tails "T", with "H" causing motion to the right, and "T" causing motion to the left. Let there be N such coin tosses, let i be the number of times "H" comes up and j denote the number of times "T" comes up. Thus, the progress of the particle, which we define as net motion to the right, is given by $(i-j)\lambda$. Letting $k = i-j$, this is just $k\lambda$. Thus, we need to know what the probability is for obtaining a particular value of k in a very large number N of coin tosses. Denote this $P(k)$.

In N coin tosses, the total number of possible sequences of "H" and "T" is 2^N. However, the number of ways we can obtain i heads and \)j\) tails, with $i+j=N$ is a binomial coefficient $N!/i!j!$. Now

$$j = N - i = N - (j+k) = N - j - k \tag{1.6.27}$$

so that $j = (N-k)/2$. Similarly,

$$i = N - j = N - (i-k) = N - i + k \tag{1.6.28}$$

so that $i = (N+k)/2$. Thus, the probability $P(k)$ is

$$P(k) = \frac{N!}{2^N i!j!} = \frac{1}{2^N}\frac{N!}{\left(\frac{N+k}{2}\right)!\left(\frac{N-k}{2}\right)!} \tag{1.6.29}$$

We now take the logarithm of both sides:

$$\ln P(k) = \ln N! - \ln 2^N - \ln\left(\frac{N+k}{2}\right)! - \ln\left(\frac{N-k}{2}\right)! \tag{1.6.30}$$

and use Stirling's approximation:

$$\ln N! \approx N\ln N - N \tag{1.6.31}$$

and write $\ln P(k)$ as

$$\begin{aligned}
\ln P(k) &\approx N\ln N - N - N\ln 2 - \frac{1}{2}(N+k)\ln\frac{1}{2}(N+k) + \frac{1}{2}(N+k) && (1.6.32)\\
&\quad - \frac{1}{2}(N-k)\ln\frac{1}{2}(N-k) + \frac{1}{2}(N-k)\\
&= N\ln N - N\ln 2 + \frac{1}{2}(N+k)\ln\frac{1}{2} - \frac{1}{2}(N+k)\ln(N+k) && (1.6.33)\\
&\quad - \frac{1}{2}(N-k)\ln\frac{1}{2} - \frac{1}{2}(N-k)\ln(N-k)\\
&= N\ln N - N\ln 2 + \frac{1}{2}(N+k)\ln 2 - \frac{1}{2}(N+k)\ln(N+k) && (1.6.34)\\
&\quad + \frac{1}{2}(N-k)\ln 2 - \frac{1}{2}(N-k)\ln(N-k)\\
&= N\ln N - \frac{1}{2}\left[(N+k)\ln(N+k) + (N-k)\ln(N-k)\right] && (1.6.35)
\end{aligned}$$

Now, write

$$\ln(N+k) = \ln N\left(1+\frac{k}{N}\right) = \ln N + \ln\left(1+\frac{k}{N}\right) \tag{1.6.36}$$

and

$$\ln(N-k) = \ln N\left(1-\frac{k}{N}\right) = \ln N + \ln\left(1-\frac{k}{N}\right) \tag{1.6.37}$$

We now use the expansions

$$\ln\left(1+\frac{k}{N}\right) = \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots \tag{1.6.38}$$

$$\ln\left(1-\frac{k}{N}\right) = -\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots \tag{1.6.39}$$

If we stop at the second-order term, then

$$\ln P(k) = N\ln N - \frac{1}{2}(N+k)\left[\ln N + \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \tag{1.6.40}$$

$$- \frac{1}{2}(N-k)\left[\ln N - \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right]$$

$$= -\frac{1}{2}(N+k)\left[\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] + \frac{1}{2}(N-k)\left[\left(\frac{k}{N}\right) + \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \tag{1.6.41}$$

$$= \frac{1}{2}N\left(\frac{k}{N}\right)^2 - k\left(\frac{k}{N}\right) \tag{1.6.42}$$

$$= \frac{k^2}{2N} - \frac{k^2}{N} = -\frac{k^2}{2N} \tag{1.6.43}$$

so that

$$P(k) = e^{-k^2/2N} \tag{1.6.44}$$

Now, if we let $x = k\lambda$ and $L = \sqrt{N}\lambda$, and if we let x be a continuous random variable, then the corresponding probability distribution $P(x)$ becomes

$$P(x) = \frac{1}{L\sqrt{2\pi}}\, e^{-x^2/2L^2} = \frac{1}{\sqrt{2\pi N\lambda^2}}\, e^{-x^2/2N\lambda^2} \tag{1.6.45}$$

which is a simple Gaussian distribution. Now, N is the number of collisions, which is given by γt, so we can write the probability distribution for the particle to diffuse a distance x in time t as

$$P(x,t) = \frac{1}{\sqrt{2\pi\gamma t\lambda^2}}\, e^{-x^2/2\gamma t\lambda^2} \tag{1.6.46}$$

Define $D = \gamma\lambda^2/2$ as the *diffusion constant*, which has units of (length)^2/time. The distribution then becomes

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\, e^{-x^2/4Dt} \tag{1.6.47}$$

Note that this distribution satisfies the following equation:

$$\frac{\partial}{\partial t}P(x,t) = D\frac{\partial^2}{\partial x^2}P(x,t) \tag{1.6.48}$$

which is called the *diffusion equation*. The diffusion equation is, in fact, more general than the Gaussian distribution in Equation 1.6.47. It is capable of predicting the distribution in any one-dimensional geometry subject to any initial distribution $P(x,0)$ and any imposed boundary conditions.

In three dimensions, we consider the three spatial directions to be independent, hence, the probability distribution for a particle to diffuse to a location $\mathbf{r} = (x,y,z)$ is just a product of the three one-dimensional distributions:

$$\mathcal{P}(\mathbf{r}) = P(x)\,P(y)\,P(z) = \frac{1}{(4\pi Dt)^{3/2}}\, e^{-(x^2+y^2+z^2)/4Dt} \tag{1.6.49}$$

and if we are only interested in diffusion over a distance r, we can introduce spherical coordinates, integrate over the angles, and we find that

$$P(r,t) = \frac{4\pi}{(4\pi Dt)^{3/2}} E^{-r^2/4Dt} \tag{1.6.50}$$

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1.7: Introduction to diffusion

An Ideal Gas of Monatomic Distinguishable Particles

The energy levels for an ideal gas in a three-dimensional cubic infinite square well of volume V are

$$E_j(N,V) = E_{\mathbf{n}_1 \cdots \mathbf{n}_N}(N,V) = \frac{\hbar^2 \pi^2}{2mV^{2/3}} \sum_{i=1}^{N} |\mathbf{n}_i|^2 \tag{1.7.1}$$

Since the particles do not interact, this sum, like the single particle in a three-dimensional box, is just a sum of $3N$ independent terms:

$$E_j(N,V) = E_{n_{x_1},n_{y_1},n_{z_1},n_{x_2},n_{y_2},n_{z_2},\cdots,n_{x_N},n_{y_N},n_{z_N}} \tag{1.7.2}$$

$$= \frac{\hbar^2 \pi^2}{2mV^{2/3}} \left(n_{x_1}^2 + n_{y_1}^2 + n_{z_1}^2 + n_{x_2}^2 + n_{y_2}^2 + n_{z_2}^2 + \cdots + n_{x_N}^2 + n_{y_N}^2 + n_{z_N}^2\right) \tag{1.7.3}$$

Since the partition function for a single particle in a cubic box (here denoted $q(V,T)$) could be written as

$$q(V,T) = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta \hbar^2 \pi^2 (n_x^2+n_y^2+n_z^2)/2mV^{2/3}} \tag{1.7.4}$$

$$= \left(\sum_{n=1}^{\infty} e^{-\beta \hbar^2 \pi^2 n^2/2mV^{2/3}} \right)^3 \tag{1.7.5}$$

$$= \left(\int_0^{\infty} e^{-\beta \hbar^2 \pi^2 n^2/2mV^{2/3}} \, dn \right)^3 \tag{1.7.6}$$

$$= \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} V \tag{1.7.7}$$

The partition function for N particles in a cubic box is just

$$Q(N,V,T) = \left(\sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta \hbar^2 \pi^2 (n_x^2+n_y^2+n_z^2)/2mV^{2/3}} \right)^N \tag{1.7.8}$$

$$= [q(V,T)]^N \tag{1.7.9}$$

$$= \left[\frac{m}{2\pi\beta\hbar^2} \right]^{3/2} V^N \tag{1.7.10}$$

The total energy of the gas is then given by

$$E = -\frac{\partial}{\partial \beta} \ln Q = \frac{3}{2} N k_B T = \frac{3}{2} nRT \tag{1.7.11}$$

The pressure is given by

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right) = \frac{N k_B T}{V} \tag{1.7.12}$$

which can be rearranged to read

$$PV = N k_B T = nRT \tag{1.7.13}$$

which is the equation of state of an ideal gas. Thus, starting from a microscopic description of the system in terms of energy levels, we are able to predict the correct thermodynamics for an ideal gas.

An Ideal Gas of Monatomic Indistinguishable particles

Boltzmann particles

In a monatomic ideal gas, the quantum spin degree of freedom is the only truly quantum property of a particle with no classical analog. If we neglect the spin degree of freedom of particles in a monatomic gas, then there is essentially no difference between a classical and a quantum monatomic ideal gas. This means that the calculation of the partition function will overcount the number of

microscopic states by $N!$ and Equation ??? needs to be divided by $N!$ to generate the correct counting for indistinguishable particles:

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!} \tag{1.7.14}$$

From Equation ???, we see that the partition function for indistinguishable monatomic Boltzmann ideal-gas particles is

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2} V^N \tag{1.7.15}$$

Note, however, that this partition function gives the same energy and pressure as in Equations 1.7.11 and 1.7.12, respectively, for distinguishable particles.

Accounting for spin: Fermions and bosons

The Boltzmann particles considered in the last subsection do not actually exist in nature. In reality, all particles carry the quantum spin degree of freedom. Neglect of spin is just an approximation, which is, nevertheless, often an accurate one. However, in many cases, we cannot neglect spin, and when spin must be included, the calculation of the partition function becomes significantly more difficult. We will not carry out the calculation in detail, but we will explore what it is that makes the problem difficult.

In nature, the spin of a particle can have either an integer or half-integer value. Particles with integer spin are called *bosons* (after the Indian physicist Satyendra Bose), while those with half-integer spin are called *fermions* (after the Italian physicist Enrico Fermi). Fermions are governed by the Pauli exclusion principle, which states that no two fermions can occupy the same quantum state. Bosons, on the other hand, have no such restriction. It is, therefore, clear that state occupancy is the key distinguishing feature between the two types of particles, and therefore, we need to express the energy of a system of fermions or bosons in terms of these state occupancies.

Recall that the energy for one particle in a cubic box is

$$\mathcal{E}_{\mathbf{n}} = \frac{\hbar^2\pi^2}{2mV^{2/3}}|\mathbf{n}| \tag{1.7.16}$$

The energy $\mathcal{E}_{\mathbf{n}}$ is called a *single-particle energy level*. Now if there are $f_{\mathbf{n}}$ particles occupying this energy level, then the contribution of this energy level to the total energy must be $\mathcal{E}_{\mathbf{n}}f_{\mathbf{n}}$. The number $f_{\mathbf{n}}$ is called an *occupation number* for the state with energy $\mathcal{E}_{\mathbf{n}}$. The total energy of a system is now obtained simply by summing over all of the single-particle levels. The total energy is now characterized by the complete set of occupation numbers, which we will denote simply as f. Thus,

$$E_f = \sum_{\mathbf{n}} \mathcal{E}_{\mathbf{n}} f_{\mathbf{n}} \tag{1.7.17}$$

Note, however, that there is a restriction on the choice of occupation numbers, namely, that the occupation numbers must sum to the total number of particles N:

$$\sum_{\mathbf{n}} f_{\mathbf{n}} = N \tag{1.7.18}$$

For fermions, the only allowable values for any one occupation number $f_{\mathbf{n}}$ is 0 or 1, consistent with the Pauli exclusion principle. However, for bosons, $f_{\mathbf{n}}$ can take on any value between 0 and N. In principle, the partition function can be computed by summing over all possible values of the occupation numbers as follows:

$$Q(N,V,T) = \sum_f e^{-\beta E_f} = \sum_f e^{-\beta\sum_{\mathbf{n}}\mathcal{E}_{\mathbf{n}}f_{\mathbf{n}}} \tag{1.7.19}$$

However, the sum over f must be carried out subject to the restriction in Equation 1.7.18, and this makes the calculation of partition functions for fermions and bosons highly nontrivial. It also makes the thermodynamics of fermionic and bosonic ideal gases nontrivial as well. In fact, there is no exact solution to either problem. At very high temperatures, it can be shown that these gases behave approximately as classical ideal gases, which means that at high temperatures, the effect of the spin degree of freedom can be safely neglected. For many systems ``high temperature" can simply mean room temperature! However, at low temperatures, where quantum effects become extremely important, the deviation from classical ideal gas behavior is significant.

At low temperatures, an ideal electron gas (electrons are spin-1/2 particles) behaves somewhat like the quasi-free conduction electrons in a metal. At low temperatures, an ideal boson gas exhibits a phenomenon known as *Bose-Einstein* condensation, in which all of the particles "condense" into the ground state. Bose-Einstein condensation is at the heart of phenomena such as superconductivity and superfluidity. If you have an interest in learning more about quantum ideal gases, see Lecture 18.

An Ideal Gas of Indistinguishable Diatomic Molecules

We will now consider an ideal gas of diatomic molecules. Each atom in a molecule consists of two nuclei and a distribution of electrons. Let r_{eq} be the equilibrium bond length of the molecule. We will assume that the spin of the nuclei can be safely neglected. In addition, we will assume that the Born-Oppenheimer approximation holds so that there is an approximate separation of nuclear and electronic energy levels, and the nuclear energy levels must be computed on each electronic Born-Oppenheimer surface. This is illustrated in the figure below:

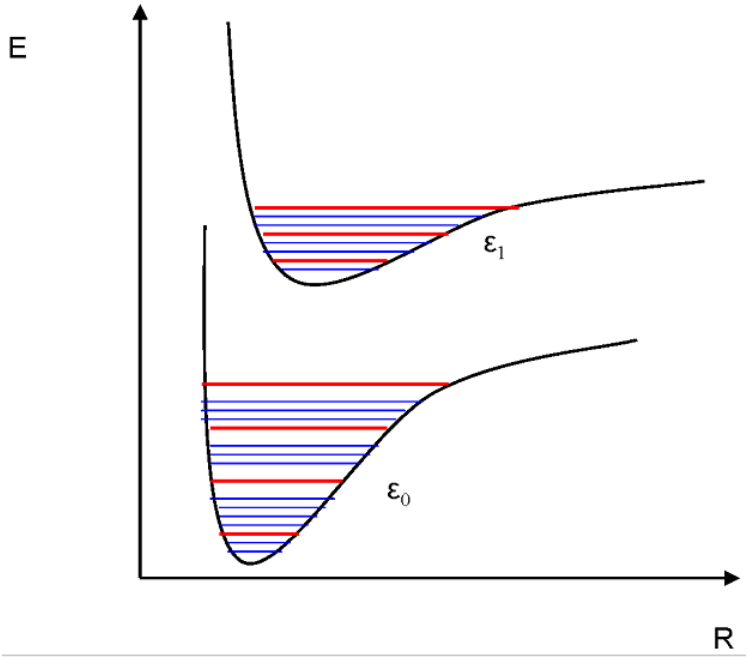


FIG 7.1: Illustration of two bonding Born-Oppenheimer electronic surfaces with nuclear levels. Rotational levels in blue, vibrational levels in red.

Note that a diatomic molecule, which has two atoms, has a total of $3 \times 2 = 6$ degrees of freedom. Three of these will be overall translations of the molecule in the box, two will be rotations of the molecule about an arbitrarily chosen axis, and the remaining degree of freedom is motion along the bond axis of the molecule.

Consider first the classical energy of the two nuclei. If the nuclei have momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ and positions $\mathbf{r}_1$ and $\mathbf{r}_2$, then the classical energy is

$$\mathcal{E}_{\text{nuc}} = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + u\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) \tag{1.7.20}$$

From this expression, it would seem that the two atoms in each molecule are inextricably coupled because the potential u is a function of the distance $|\mathbf{r}_1 - \mathbf{r}_2|$ between them. However, the energy can, in fact, be separated into independent contributions by a simple change of variables. In particular, we transform to center-of-mass and relative coordinates by the following change of variables:

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M} \tag{1.7.21}$$

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 \tag{1.7.22}$$

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{1.7.23}$$

$$\mathbf{p} = \frac{m_2\mathbf{p}_1 - m_1\mathbf{p}_2}{M} \tag{1.7.24}$$

where $M = m_1 + m_2$. Here $\mathbf{R}$ and $\mathbf{P}$ are the center of mass position and momentum, respectively, while $\mathbf{r}$ and $\mathbf{p}$ are the relative coordinate and momentum, respectively. The transformation can be inverted to give

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r} \tag{1.7.25}$$

$$\mathbf{p}_1 = \frac{m_1}{M}\mathbf{P} + \mathbf{p} \tag{1.7.26}$$

$$\mathbf{r}_2 = \mathbf{R} + \frac{m_1}{M}\mathbf{r} \tag{1.7.27}$$

$$\mathbf{p}_2 = \frac{m_2}{M}\mathbf{P} - \mathbf{p} \tag{1.7.28}$$

Substituting these into the expression for $\mathcal{E}_{\text{nuc}}$, we obtain

$$\mathcal{E}_{\text{nuc}} = \frac{1}{2m_1}\left(\frac{m_1}{M}\mathbf{P}+\mathbf{p}\right)^2 + \frac{1}{2m_2}\left(\frac{m_2}{M}\mathbf{P}-\mathbf{p}\right)^2 + u(r) \tag{1.7.29}$$

$$= \frac{1}{2m_1}\left(\frac{m_1^2}{M^2}\mathbf{P}^2 + \frac{2m_1}{M}\mathbf{P}\cdot\mathbf{p} + \mathbf{p}^2\right) + \frac{1}{2m_2}\left(\frac{m_1^2}{M^2}\mathbf{P}^2 - \frac{2m_1}{M}\mathbf{P}\cdot\mathbf{p} + \mathbf{p}^2\right) \tag{1.7.30}$$

$$= \frac{m_1}{2M^2}\mathbf{P}^2 + \frac{m_2}{2M^2}\mathbf{P}^2 + \frac{1}{M}\mathbf{P}\cdot\mathbf{p} - \frac{1}{M}\mathbf{P}\cdot\mathbf{p} + \frac{\mathbf{p}^2}{2m_1} + \frac{\mathbf{p}^2}{2m_2} \tag{1.7.31}$$

$$= \frac{m_1+m_2}{2M^2}\mathbf{P}^2 + \frac{1}{2}\frac{m_1+m_2}{m_1m_2}\mathbf{p}^2 \tag{1.7.32}$$

We define

$$\mu = \frac{m_1m_2}{m_1+m_2} \tag{1.7.33}$$

which is called the *reduced mass*. In terms of M and μ, the energy can be expressed as

$$\mathcal{E}_{\text{nuc}} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + u(r) \tag{1.7.34}$$

From this we see that the energy due to center-of-mass motion is purely kinetic. This term gives the energy of simple translations of the molecule throughout the box. The remaining term is purely internal motion of the molecule, called *relative* motion. Thus, we see that the energy is now separated into purely translational and relative contributions, and we write

$$\mathcal{E}_{\text{nuc}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{rel}} \tag{1.7.35}$$

Now for the relative motion, we resolve the vector $\mathbf{p}$ into a radial component $\mathbf{p}_r$ and a residual two-dimensional momentum in the two angular directions (θ, ϕ), i.e., $\mathbf{p}_{(\theta,\phi)}$. The first component $\mathbf{p}_r$ is a purely radial momentum directed radial outward from the origin. The remaining two components describe rotational motion in the azimuthal (ϕ) and polar ((\theta\)) directions. These two components are perpendicular so that $\mathbf{p}_r \cdot \mathbf{p}_{(\theta,\phi)} = 0$. In this case, the relative energy becomes

$$\mathcal{E}_{\text{rel}} = \frac{\mathbf{p}_r^2}{2\mu} + \frac{\mathbf{p}_{(\theta,\phi)}^2}{2\mu} + u(r) \tag{1.7.36}$$

The purely radial part contains the two terms $\mathbf{p}_r^2/2\mu + u(r)$. This motion occurs entirely along the direction of the bond axis and constitutes the vibrational energy. The remaining purely kinetic term is the rotational motion of the molecule. Thus, we can write the relative energy as

$$\mathcal{E}_{\text{rel}} = \mathcal{E}_{\text{vib}} + \mathcal{E}_{\text{rot}} \tag{1.7.37}$$

so that the total nuclear energy of the molecule becomes

$$\mathcal{E}_{\text{nuc}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{rot}} + \mathcal{E}_{\text{vib}} \tag{1.7.38}$$

Note that there is an approximation made here, namely, that rotations and vibrations are not coupled in any way. The approximation we are making here is that rotations are sufficiently slow compared to vibrations that we can consider the molecule as a rigid rotor of length r_{eq}, where r_{eq} is the equilibrium bond length. If the vibrations are sufficiently fast, then on the time scale of rotations, the average distance between the atoms will be r_{eq}, hence, the approximation is a reasonable one, but it must be kept in mind that this is what we are assuming.

Let us now construct the nuclear part of the partition function for a single molecule. The translational energy is just that of the center of mass, and hence, its energy levels are those of a particle of mass M in a box of volume V, characterized by the usual quantum number $\mathbf{n} = (n_x, n_y, n_z)$:

$$\mathcal{E}_{\mathbf{n}}^{\text{trans}} = \frac{\hbar^2 \pi^2}{2MV^{2/3}} |\mathbf{n}|^2 \tag{1.7.39}$$

For the rotational energy, we consider rotations of the molecule about an axis through the position $\mathbf{r}_1$ of atom $\mathbf{1}$. In this case, the moment of inertia introduced in the last lecture is just $I = \mu r_{\text{eq}}^2$. The two quantum numbers we need for rotation are J and m_J, where $J = 0, 1, 2, ...$, and $m_J = -J, -J+1, \ldots, J-1, J$. The energy levels are then given by

$$\mathcal{E}_{\text{rot}} = \frac{\hbar^2}{2I} J(J+1) \tag{1.7.40}$$

Finally, there is the vibrational motion, the potential energy of which is $u(r)$. Typically, $u(r)$ resembles the plot shown in the figure below:

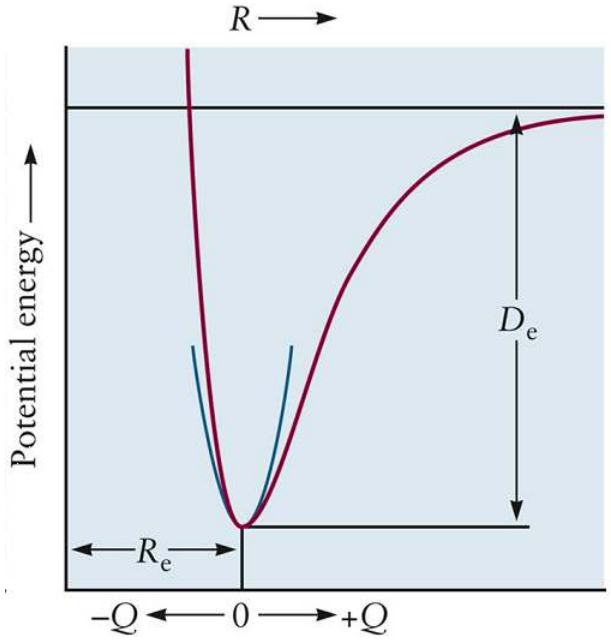


FIG 7.2: Typical shape of $u(r)$ for a covalent bond, and the harmonic approximation to the curve.

If the temperature of the gas is sufficiently low, then only the lowest lying vibrational energy levels are important, and we can approximate the true vibrational potential with a harmonic potential (see figure) of natural frequency ω and write

$$u(r) = \frac{1}{2} \mu \omega^2 \left(r - r_{\text{eq}}\right)^2 \tag{1.7.41}$$

For a harmonic oscillator, the energy levels are given by

$$\mathcal{E}_{\nu}^{\text{vib}} = \left(\nu + \frac{1}{2}\right) \hbar\omega, \qquad \nu = 0, 1, 2, ... \tag{1.7.42}$$

The six quantum numbers $(n_x, n_y, n_z, J, m_J, \nu)$ correspond to the six degrees of freedom we identified at the beginning of this section. The complete nuclear energy levels can now be expressed as

$$\mathcal{E}_{n_x\, n_y\, n_z\, J\, m_J\, \nu} = \mathcal{E}_{\mathbf{n}\, J\, m_J\, \nu} \frac{\hbar^2 \pi^2}{2MV^{2/3}} |\mathbf{n}|^2 + \frac{\hbar^2}{2I} J(J+1) + \left(\nu + \frac{1}{2}\right) \hbar\omega \tag{1.7.43}$$

Given these energy levels, we can construct the corresponding energy levels for a system of N non-interacting diatomics as

$$E_{\mathbf{n}_1\, J_1\, m_{J_1}\, \nu_1\, \mathbf{n}_2\, J_2\, m_{J_2}\, \nu_2 \cdots \mathbf{n}_N\, J_N\, m_{J_N}\, \nu_N} \tag{1.7.44}$$
$$= \sum_{i=1}^{N} \frac{\hbar^2 \pi^2}{2MV^{2/3}} |\mathbf{n}_i|^2 + \frac{\hbar^2}{2I} J_i(J_i+1) + \left(\nu_i + \frac{1}{2}\right) \hbar\omega$$

Since the energy levels are just a sum of single-molecule energy levels, Equation 1.7.14 applies, and we can write the total partition function as

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!} \tag{1.7.45}$$

where $q(V,T)$ is the single-molecule partition function corresponding to the energy levels in Equation???.

The nuclear partition function for one molecule is

$$q_{\text{nuc}}(V,T) = \sum_{\mathbf{n}} \sum_{J=0}^{\infty} \tag{1.7.46}$$
$$\sum_{m_J=-J}^{J} \sum_{\nu=0}^{\infty} \exp\left\{-\beta\left[\frac{\hbar^2\pi^2}{2MV^{2/3}}|\mathbf{n}|^2 + \frac{\hbar^2}{2I}J(J+1) + \left(\nu+\frac{1}{2}\right)\hbar\omega\right]\right\}$$
$$= \left(\sum_{\mathbf{n}} \exp\left[-\frac{\beta\hbar^2\pi^2}{2MV^{2/3}}|\mathbf{n}|^2\right]\right)\left(\sum_{J=0}^{\infty}\sum_{m_J=-J}^{J} \exp\left[-\frac{\beta\hbar^2}{2I}J(J+1)\right]\right) \tag{1.7.47}$$
$$\left(\sum_{\nu=0}^{\infty} \exp\left[-\beta\left(\nu+\frac{1}{2}\right)\hbar\omega\right]\right)$$
$$= q_{\text{trans}}(V,T)\, q_{\text{rot}}(T)\, q_{\text{vib}}(T) \tag{1.7.48}$$

Here

$$\sum_{\mathbf{n}} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \tag{1.7.49}$$

Each of these partition functions were worked out in the previous lecture, so if we simply take over those results, we obtain the nuclear partition function as

$$q_{\text{nuc}}(V,T) = \left[V\left(\frac{M}{2\pi\beta\hbar^2}\right)\right]\left[\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right]\left[\frac{1}{2\pi\beta\hbar B}\right] \tag{1.7.50}$$

where $B = \hbar/(4\pi I)$ is called the *rotation constant*. Remember that for the translational and rotational partition functions, we approximated the energy levels as a continuum so that the sums could be replaced by integrals.

The final energy term we need is the electronic energy. Recall that, within the Born-Oppenheimer approximation, each electronic energy surface, assuming that it has bonding rather than anti-bonding character, gives rise to a set of rotational and vibrational energy levels (translational energies are independent of the particular electronic surface). Let the global minima on these bonding surfaces be denoted $\mathcal{E}_0^{(\text{elec})}$, $\mathcal{E}_1^{(\text{elec})}$, ... As a reference energy, we choose the value of $\mathcal{E}_0^{(\text{elec})}$ and define each of the electronic energies relative to these, i.e., $\mathcal{E}_{10}^{(\text{elec})} = \mathcal{E}_1^{(\text{elec})} - \mathcal{E}_0^{(\text{elec})}$, $\mathcal{E}_{20}^{(\text{elec})} = \mathcal{E}_2^{(\text{elec})} - \mathcal{E}_0^{(\text{elec})}$, and so forth. If the degeneracies of these levels are g_0, g_1, g_2,..., then the electronic contribution to the partition function is

$$q_{\text{elec}}(T) = g_0 + g_1 e^{-\beta\mathcal{E}_{10}^{(\text{elec})}} + g_2 e^{-\beta\mathcal{E}_{20}^{(\text{elec})}} + \cdots \tag{1.7.51}$$

Generally, the electronic energy differences are so large at ordinary temperatures that the above sum converges after just a few terms. Often, we only need one or two terms in the above.

Putting everything together, we can write the partition function for the full N-particle ideal gas system as

$$Q(N,V,T) \tag{1.7.52}$$
$$= \frac{1}{N!}\left[V\left(\frac{M}{2\pi\beta\hbar^2}\right)\right]^N \left[\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right]^N \left[\frac{1}{2\pi\beta\hbar B}\right]^N \left[g_0 + g_1 e^{-\beta\mathcal{E}_{10}^{(\text{elec})}} + g_2 e^{-\beta\mathcal{E}_{20}^{(\text{elec})}} + \cdots\right]^N$$

From this partition function, we can compute the thermodynamic properties of an ideal gas of indistinguishable diatomic molecules.

First the pressure is given by

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right) \tag{1.7.53}$$

$$= \frac{N k_B T}{V} \tag{1.7.54}$$

which is equivalent to the ideal gas law $PV = Nk_BT = nRT$. Note that none of the internal properties of the molecules have any effect on the equation of state, which arises entirely from translational motion, this being the only volume-dependent contribution.

The energy is given by

$$E = -\frac{\partial \ln Q}{\partial \beta} \tag{1.7.55}$$

$$= \frac{3}{2} N k_B T + \frac{1}{2} N \hbar \omega + \frac{N \hbar \omega}{e^{\beta \hbar \omega} - 1} + N k_B T + \frac{N \left(g_1 \mathcal{E}_{10}^{(\text{elec})} e^{-\beta \mathcal{E}_{10}^{(\text{elec})}} + \cdots \right)}{g_0 + g_1 e^{-\beta \mathcal{E}_{10}^{(\text{elec})}} + \cdots} \tag{1.7.56}$$

$$= \frac{5}{2} N k_B T + \frac{1}{2} N \hbar \omega + \frac{N \hbar \omega}{e^{\beta \hbar \omega} - 1} + \frac{N \left(g_1 \mathcal{E}_{10}^{(\text{elec})} e^{-\beta \mathcal{E}_{10}^{(\text{elec})}} + \cdots \right)}{g_0 + g_1 e^{-\beta \mathcal{E}_{10}^{(\text{elec})}} + \cdots} \tag{1.7.57}$$

Calculating Partition Functions for Fully Interacting Systems using Feynman's Path Integral

The reason we can only discuss partition functions for the ideal gas is that it is nearly impossible to calculate energy levels for anything but the simplest systems, basically at the level of ideal gases. As we discussed in Lecture 4, the effort to solve the Schrödinger equation for systems with more than just a few atoms grows exponentially with the number of atoms.

As it happens, there is a way to compute the partition function and thermodynamic properties of systems containing thousands of atoms, which is often sufficiently large to approach the thermodynamic limit. This approach is based on a reformulation of quantum mechanics due to Feynman.

In order to introduce Feynman's approach, let us consider the expression for the partition function once again:

$$Q(N,V,T) = \sum_j e^{-\beta E_j(N,V)} \tag{1.7.58}$$

Recall that the energy levels $E_j(N,V)$ are eigenvalues of the Hamiltonian $\hat{H}$. Once we know the eigenvalues of $\hat{H}$, then $\hat{H}$ can be represented as a diagonal matrix with the eigenvalues on the diagonal. Interestingly, if we take the Hamiltonian and form the object $\exp(-\beta\hat{H})$, the quantities $\exp(-\beta E_j(N,V))$ are *its* eigenvalues. Thus, when we compute the sum in Equation 1.7.58, we are actually taking the trace of the matrix $\exp(-\beta\hat{H})$. In general, the trace of any matrix A_{ij} is

$$\text{Tr}(A) = \sum_i A_{ii} \tag{1.7.59}$$

That is, we just need to sum over the diagonal elements of the matrix. A key property of traces is that they are the same no matter how we represent the matrix A. We do not need its eigenvalues, and we do not need A to be diagonal. Rather, we can use the positions of the quantum particles to compute the needed trace. Let $X = \mathbf{r}_1, \ldots, \mathbf{r}_N$ represent the set of particle positions. Then, we can calculate the trace of $\exp(-\beta\hat{h})$ as

$$Q(N,V,T) = \text{Tr}\left[e^{-\beta\hat{H}} \right] = \int dX \left[e^{-\beta\hat{H}} \right]_{XX} \tag{1.7.60}$$

Note that because the positions are continuous rather than discrete variables, when we express the trace in terms of X, we must do so as an integral rather than as a sum.

Feynman, who was born right here in Far Rockaway, devised a remarkably elegant way to calculate $[\exp(-\beta\hat{H})]_{XX}$. By multiplying and dividing the argument of the exponential by $\hbar$, we obtain

$$Q(N,V,T) = \int dX \left[e^{-\beta\hbar\hat{H}/\hbar} \right]_{XX} \tag{1.7.61}$$

Note that the quantity $\beta\hbar$ has units of time. Feynman recognized that this is no mere accident or coincidence. His key insight was to recognize that $\exp[-\beta\hat{H}]_{XX}$ could be computed by considering some path, $X(t)$, parameterized by time, that the system could take that starts at X at time $t = 0$, returns to X in time $T = \beta\hbar$, but that can go anywhere in space between $t = 0$ and $t = \beta\hbar$. These are known as *cyclic paths*. This is illustrated in the figure below:

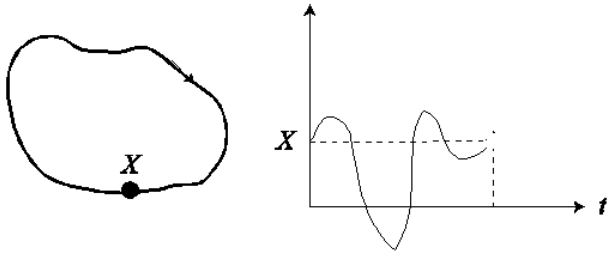


FIG 7.3: Illustration of the Feynman path integral. Left: Cartoon of a path, beginning and ending at the point X. Right: Path in the $X - t$ plane.

Let this path be denoted $X(t) = (\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t))$. Then Feynman showed that $\exp[-\beta\hat{H}]_{XX}$ could be computed in terms of an integral of the energy, expressed as a function of positions and velocities, over the path:

$$\left[e^{-\beta\hbar\hat{H}/\hbar}\right]_{XX} = \exp\left[\frac{1}{\hbar}\int_0^{\beta\hbar}\left(\frac{1}{2}\sum_{i=1}^{N} m_i v_i^2(t) + U(\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t))\right) dt\right] \tag{1.7.62}$$

This is why the technique is called a *path integral*. Let us denote the integral in the above expression as S:

$$S = \int_0^{\beta\hbar}\left(\frac{1}{2}\sum_{i=1}^{N} m_i v_i^2(t) + U(\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t))\right) dt \tag{1.7.63}$$

Then, the partition function can be computed by summing over *all* possible paths that take the system from X back to X in time $\beta\hbar$:

$$Q(N, V, T) = \sum_{\text{paths}} e^{-S/\hbar} \tag{1.7.64}$$

The need to include *all* possible paths is a consequence of the uncertainty principle. If we have full knowledge of the positions $X(t)$ along a path for all t, then we have no knowledge of the momenta. However, classically, a definite path has specific values of positions *and* momenta simultaneously. Without knowledge of momenta, the particles could follow any path from X to X, and because of the uncertainly, we must consider all of them.

The key to the use of Equation 1.7.64 is to discretize the paths into P time intervals, each having a time step or interval $\beta\hbar P$. Once these paths are discretized, the sum can be carried out on a computer with a computational cost no more than P times what it would cost to carry out the calculation using classical mechanics. The basic scheme is shown in the figure below for $P = 5$ and two interacting quantum particles. Notice that when the paths are discretized, neighboring points on each cyclic path are connected by harmonic springs.

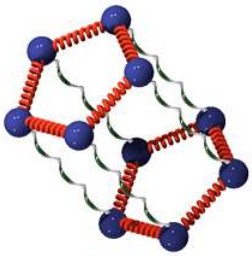


FIG 7.4: Path integral for two particles discretized into $P = 5$ time intervals. Interactions are computed between points in the same time interval only.

In the figures that follow, we show three examples of the path integral approach. The first is an example of a simple organic molecule, malonaldehyde, shown with an internal hydrogen bond. Because of the internal bond, a proton on one of the OH groups can transfer through the bond to the neighboring oxygen. The energetic barrier to this reaction is approximately 14.23 kJ/mol. However, recall that quantum mechanics allows for a phenomenon known as *tunneling*, which gives particles a non-zero

probability to be located in classically forbidden regions. In malonaldehyde, tunneling largely dominates this internal proton transfer, thus causing a substantial reduction in the effective energy barrier, which we will learn is equivalent to the *free energy* barrier, from **14.23** kJ/mol to about **6.7** kJ/mol. The figure shows what a tunneling path looks like. We see that when the proton tunnels, it exists in a Schrödinger's cat-like state in which it is simultaneously bonded to both oxygens, and only an observation of the proton can localize it on one oxygen or the other.

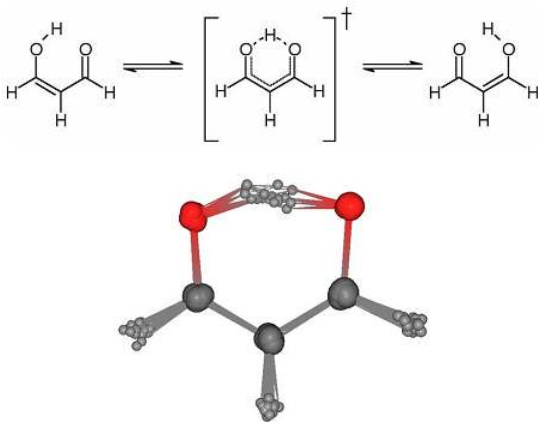


FIG 7.5: Top: Illustration of the internal proton transfer reaction in malonaldehyde. Bottom: A tunneling path in malonaldehyde.

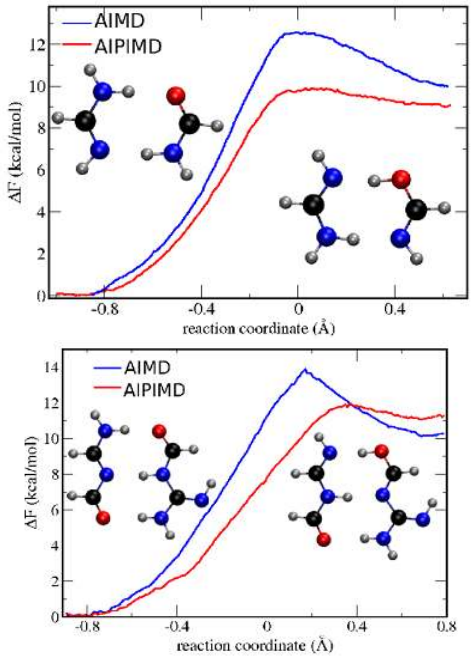


FIG 7.6: left: Model of the AT base pair and reaction free energy profile. right: Same for GC base pair.

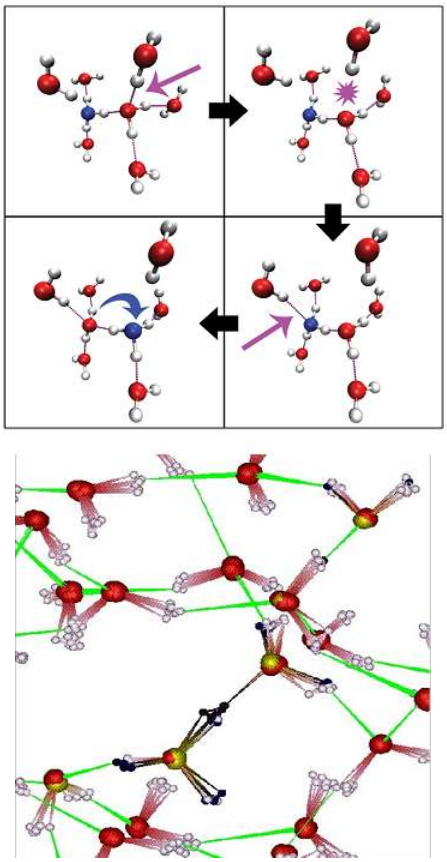


FIG 7.7: left: Schematic of the hydronium diffusion mechanism showing concerted hydrogen bond breaking and forming events. right: A particular path showing the delocalization of the topological defect in the hydrogen bond network *of the solution.*

The second example concerns the occurrence of rare tautomers in DNA base pairs. The two strands of DNA are held together by hydrogen bonds formed between pairs of nucleotide bases. The so-called tautomeric shift problem occurs when the protons in the hydrogen bonds holding a pair of bases together transfer through the hydrogen bonds. It was posited that if the protons become stuck in their shifted positions at the time of DNA replication, the incorrect locations of the protons would cause mispairing when the DNA replicates itself, which could lead to diseases such as cancer. The implication of this supposition is that quantum mechanics, which allows the protons to tunnel into their shifted positions, is the evil force behind such afflictions. However, experiments were never able to see the spontaneous formation of such rare tautomers, and a satisfactory explanation as to why took several decades to emerge. In fact, if we study this tautomeric shift problem using the Feynman path integral, and plot the reaction free energy profiles, the answer becomes clear. In the figure, we see two curves in the reaction profiles. One treats the protons as classical particles, and the other uses a proper quantum treatment. The two reaction profiles are clearly quite different. In the classical profile, we see that it is energetically steeply uphill to go from the normal form to the rare tautomer, but once up and over the hump, there is another energetic barrier to return to the normal form. Thus, it would be possible for the system to become stuck as a rare tautomer. However, with a proper quantum treatment, we see that, while there is still a steep uphill clime to get to the tautomeric shifted form, there is absolutely no barrier to return to the normal form. Thus, if there is a rare fluctuation that takes the system to the tautomeric form, it will immediately return to the normal form, thus explaining why spontaneous formation of rare tautomers is not observed. Thus, quantum mechanics, rather than being the evil force that gives us cancer, is harnessed by nature to prevent this from occurring in the first place.

The last example is that of a bulk aqueous acid solution. We learn in freshman chemistry that acids contains excess protons in the form of hydronium (H_3O^+) ions. Hydronium, as it turns out, is a highly species in water. What makes it so mobile is the fact that it does not diffuse hydrodynamically as would water molecules in the solution. Rather, hydronium undergoes a process known as structural diffusion, in which the hydronium structure is transported as a topological defect in water's hydrogen bond network through a series of proton transfer reactions between hydronium and its first solvation-shell water molecules. This process is driven by a complex series of hydrogen bond breaking and forming events that allow the structure to migrate through the hydrogen bond

network. The basic mechanism is illustrated in the figure. However, what makes the process especially fast is the fact that the hydronium ion is a highly quantum mechanical species that can become very delocalized over the hydrogen bond network. If we examine some of the quantum paths and follow the location of the hydronium around the path, we see something strange occurring. At each point of the path, we ask where the hydronium oxygen is, and we find that at different points along the path, the hydronium oxygen is at a different site in the solution. In fact, as the figure shows, the hydronium ion can become delocalized over as many as five hydrogen bonds! By allowing the paths to become such spatially extended objects, quantum mechanics allows the system to probe the "most promising" direction for the next structural diffusion event. If this were not possible, hydronium diffusion would not be so fast, and devices such as proton-exchange-membrane fuel cells would not work as well as they do.

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1.8: Computational methods in statistical mechanics

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1.9: First law of thermodynamics and thermodynamic potentials

Consider a system of n moles in a container of volume V with a fixed internal energy E. The variables n, V, and E are all macroscopic thermodynamic quantities referred to as *control variables*. Control variables are simply quantities that characterize the ensemble and that determine other thermodynamic properties of the system. Different choices of these variables lead to different system properties. In order to describe the thermodynamics of an ensemble of systems with given values of n, V, and E, we seek a unique state function of these variables. We will now show that such a state function can be obtained from the first law of thermodynamics, which relates the energy E of a system to a quantity Q of heat absorbed and an amount of work W done on the system:

$$E = Q + W \tag{1.9.1}$$

The derivation of the desired state function begins by examining how the energy changes if a small amount of heat dQ is added to the system and a small amount of work dW is done on the system. Since E is a state function, this thermodynamic transformation may be carried out along any path, and it is particularly useful to consider a reversible path for which

$$dE = dQ_{\text{rev}} + dW_{\text{rev}} = dQ_{\text{irrev}} + dW_{\text{irrev}} \tag{1.9.2}$$

Note that since Q and W are not state functions, it is necessary to choose whether to use a reversible or irreversible path. For simplicity, let us choose the reversible ('rev') path. The amount of heat absorbed by the system can be related to the change in the entropy ΔS of the system by

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T}, \qquad dS = \frac{dQ_{\text{rev}}}{T} \tag{1.9.3}$$

where T is the temperature of the system. Therefore, $dQ_{\text{rev}} = T\,dS$. Work done on the system is measured in terms of the two control variables V and N. Let $P(V)$ be the pressure of the system at the volume V. Mechanical work can be done on the system by compressing it from a volume V_1 to a new volume $V_2 < V_1$:

$$W_{12}^{(\text{mech})} = -\int_{V_1}^{V_2} P(V)\,dV \tag{1.9.4}$$

where the minus sign indicates that work is positive in a compression. A small volume change dV corresponds to an amount of work $dW_{\text{rev}}^{(\text{mech})} = -P(V)\,dV$. Although we will typically suppress the explicit volume dependence of P on V and write simply, $dW_{\text{rev}}^{(\text{mech})} = -P\,dV$, it must be remembered that P depends not only on V but also on n and E. In addition to the mechanical work done by compressing a system, chemical work can also be done on the system by increasing the number of moles.

$$dW_{\text{rev}}^{(\text{chem})} = \mu\,dn \tag{1.9.5}$$

is done on the system. if there are M distinct chemical species, each with its own chemical potential μ_k, $k = 1, \ldots, M$, then we would express the chemical work as

$$dW_{\text{rev}}^{(\text{chem})} = \sum_{k=1}^{M} \mu_k\,dn_k \tag{1.9.6}$$

$$dW_{\text{rev}} = dW_{\text{rev}}^{(\text{mech})} + dW_{\text{rev}}^{(\text{chem})} = -P\,dV + \sum_{k=1}^{M} \mu_k\,dn_k \tag{1.9.7}$$

so that the total change in energy is

$$dE = T\,dS - P\,dV + \sum_{k=1}^{M} \mu_k\,dn_k \tag{1.9.8}$$

By writing Equation 10.8 in the form

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_{k=1}^{M} \frac{\mu_k}{T}dn_k \tag{1.9.9}$$

it is clear that the entropy is both a state function and a natural function of V, E, and $n_1, \ldots, n_M$. Since S is a function of $n_1, \ldots, n_M$, V, and E, the change in S resulting from small changes in n_k, V, and E can also be written using the chain rule as

$$dS = \left(\frac{\partial S}{\partial E}\right)_{\{n\},V} dE + \left(\frac{\partial S}{\partial V}\right)_{\{n\},E} dV + \sum_{k=1}^{M} \left(\frac{\partial S}{\partial n_k}\right)_{V,E} dn_k \tag{1.9.10}$$

Comparing Equation 10.10 with Equation 10.9 shows that the thermodynamic quantities T, P, and μ_k can be obtained by taking partial derivatives of the entropy with respect to each of the three control variables:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{\{n\},V}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{\{n\},E}, \quad \frac{\mu_k}{T} = -\left(\frac{\partial S}{\partial n_k}\right)_{V,E} \tag{1.9.11}$$

We now recall that the entropy is a quantity that can be related to the number of microscopic states of the system. This relation was first proposed by Ludwig Boltzmann in 1877, although it was Max Planck who actually formalized the connection. Let Ω be the number of microscopic states available to a system. The relation connecting S and Ω states that

$$S(n_1, \ldots, n_M, V, E) = k_B \ln \Omega(n_1, \ldots, n_M, V, E) \tag{1.9.12}$$

Since S is a function of $n_1, \ldots, n_M$, V, and E, Ω must be as well. Since we can determine $\Omega(n_1, \ldots, n_M, V, E)$ from a microscopic description of the system, Equation 10.12 then provides a connection between this microscopic description and macroscopic thermodynamic observables.

$$\frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{\{n\},V}, \quad \frac{P}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial V}\right)_{\{n\},E}, \quad \frac{\mu_k}{k_B T} = -\left(\frac{\partial \ln \Omega}{\partial n_k}\right)_{V,E} \tag{1.9.13}$$

which shows that we can start with a microscopic description of the system and obtain the thermodynamic properties of the system.

On the other hand, we also see that E is a natural function of V, S, and $n_1, \ldots, n_M$. Thus, from the chain rule, we also have

$$dE = \left(\frac{\partial E}{\partial V}\right)_{\{n\},S} dV + \left(\frac{\partial E}{\partial S}\right)_{\{n\},V} dS + \sum_{k=1}^{M} \left(\frac{\partial E}{\partial n_k}\right)_{S,V} dn_k \tag{1.9.14}$$

and comparing to Equation 10.8, we have the additional thermodynamic relations

$$T = \left(\frac{\partial E}{\partial V}\right)_{\{n\},V}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{\{n\},S}, \quad \mu_k = \left(\frac{\partial E}{\partial n_k}\right)_{V,S} \tag{1.9.15}$$

Changing Ensembles: Legendre Transforms

In thermodynamics, changing thermodynamic potentials between ensembles requires the use of a technique known as the *Legendre transform*. In order to see what a Legendre transform is, consider a simple function $f(x)$ of a single variable x. Suppose we wish to express $f(x)$ in terms of a new variable s, where s and x are related by

$$s = f'(x) \equiv g(x) \tag{1.9.16}$$

with $f'(x) = df/dx$. Can we determine $f(x)$ at a point x_0 given only $s_0 = f'(x_0) = g(x_0)$? The answer to this question, of course, is no. The reason, as Figure 10.1 makes clear, is that s_0, being the slope of the line tangent to $f(x)$ at x_0, is also the slope of $f(x) + c$ at $x = x_0$ for any constant c. Thus, $f(x_0)$ cannot be uniquely determined from

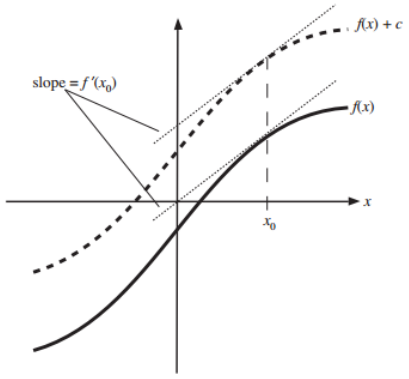


Figure 10.1: Depiction of the Legendre transform.

s_0. However, if we specify both the slope, $s_0 = f'(x_0)$, and the y-intercept, $b(x_0)$, of the line tangent to the function at x_0, then $f(x_0)$ can be uniquely determined. In fact, $f(x_0)$ will be given by the equation of the line tangent to the function at x_0:

$$f(x_0) = f'(x_0)\, x_0 + b(x_0) \tag{1.9.17}$$

Equation 10.17 shows how we may transform from a description of $f(x)$ in terms of x to a new description in terms of s. First, since Equation 10.17 is valid for all s_0, it can be written generally in terms of x as

$$f(x) = f'(x)\, x + b(x) \tag{1.9.18}$$

Then, recognizing that $f'(x) = g(x) = s$ and $x = g^{-1}(s)$, and assuming that $s = g(x)$ exists and is a one-to-one mapping, it is clear that the function $b(g^{-1}(s))$, given by

$$b(g^{-1}(s)) = f(g^{-1}(s)) - sg^{-1}(s) \tag{1.9.19}$$

contains the same information as the original $f(x)$ but expressed as a function of s instead of x. We call the function $\tilde{f}(s) = b(g^{-1}(s))$ the *Legendre transform* of $f(x)$. The function $\tilde{f}(s)$ can be written compactly as

$$\tilde{f}(s) = f(x(s)) - sx(s) \tag{1.9.20}$$

where $x(s))$ serves to remind us that x is a function of s through the variable transformation $x = g^{-1}(s)$.

The generalization of the Legendre transform to a function f of n variables $n_1, \ldots, x_n$ is straightforward. In this case, there will be a variable transformation of the form

$$s_1 = \frac{\partial f}{\partial x_1} = g_1(x_1, \ldots, x_n) \tag{1.9.21}$$

$$\vdots \tag{1.9.22}$$

$$s_n = \frac{\partial f}{\partial x_n} = g_n(x_1, \ldots, x_n) \tag{1.9.23}$$

Again, it is assumed that this transformation is invertible so that it is possible to express each x_i as a function $x_i(s_1, \ldots, s_n)$ of the new variables. The Legendre transform of f will then be

$$\tilde{f}(s_1, \ldots, s_n) = f(x_1(s_1, \ldots, s_n), \ldots, x_n(s_1, \ldots, s_n)) - \sum_{i=1}^{n} s_i x_i(s_1, \ldots, s_n) \tag{1.9.24}$$

Note that it is also possible to perform the Legendre transform of a function with respect to any subset of the variables on which the function depends.

Transforming to the Canonical Ensemble

The Legendre transformation technique introduced in the previous section is the method by which thermodynamic potentials are transformed between ensembles. What we need to do is transform from a function of V, S, and $\{n\}$ to a function of V, T, and $\{n\}$. That is, we need to transform from $E(n_1, \ldots, n_M, V, S)$ to a new energy that is a function of $n_1, \ldots, n_M, V, T$. The Legendre transform is appropriate for this operation since

$$T = \left(\frac{\partial E}{\partial S}\right)_{\{n\},V} \tag{1.9.25}$$

Applying the Legendre transform formula, we obtain a new energy

$$\tilde{E}(\{n\},V,T) = E(\{n\},V,S(\{n\},V,T)) - \frac{\partial E}{\partial S}S(\{n\},V,T) \tag{1.9.26}$$

$$= E(\{n\},V,S(\{n\},V,T)) - TS(\{n\},V,T) \tag{1.9.27}$$

The function $\tilde{E}(\{n\},V,T)$ is a new state function known as the *Helmholtz free energy* and is denoted $A(\{n\},V,T)$ or $F(\{n\},V,T)$. We will show shortly that when a thermodynamic transformation of a system from state 1 to state 2 is carried out on a system along a reversible path, then the work needed to effect this transformation is equal to the change in the Helmholtz free energy ΔA. From Equation 10.24, it is clear that A has both energetic and entropic contributions, and the delicate balance between these two contributions can sometimes have a sizeable effect on the free energy. Free energy is a particularly useful concept as it determines whether a process is thermodynamically favorable, indicated by a decrease in free energy, or unfavorable, indicated by an increase in free energy. It is important to note that although thermodynamics can determine if a process is favorable, it has nothing to say about the time scale on which the process occurs.

A process in which $n_1,\ldots,n_M$, V, and T change by small amounts dn_k, dV, and dT leads to a change dA in the Helmholtz free energy of

$$dA = \sum_{k=1}^{M}\left(\frac{\partial A}{\partial n_k}\right)_{V,T} dn_k + \left(\frac{\partial A}{\partial V}\right)_{\{n\},T} dV + \left(\frac{\partial A}{\partial T}\right)_{\{n\},V} dT \tag{1.9.28}$$

via the chain rule. However, since $A = E - TS$, the change in A can also be expressed as

$$dA = dE - S\,dT - T\,dS \tag{1.9.29}$$

$$= T\,dS - P\,dV + \sum_{k=1}^{M}\mu_k\,dn_k - S\,dT - T\,dS \tag{1.9.30}$$

$$= -P\,dV + \sum_{k=1}^{M}\mu_k\,dn_k - S\,dT \tag{1.9.31}$$

where the second line follows from the first law of thermodynamics. By comparing the last line of Equation 10.26 with Equation 10.25, we see that the thermodynamic variables obtained from the partial derivatives of A are:

$$\mu_k = \left(\frac{\partial A}{\partial n_k}\right)_{V,T}, \quad P = -\left(\frac{\partial A}{\partial V}\right)_{\{n\},T}, \quad S = -\left(\frac{\partial A}{\partial T}\right)_{\{n\},V} \tag{1.9.32}$$

Note that at constant temperature,

$$dA = -P\,dV + \sum_{k=1}^{M}\mu_k\,dn_k = dW_{\text{rev}} \tag{1.9.33}$$

which shows that, physically, the change in free energy is simply the reversible work that we would need to perform on a system in order to change its thermodynamic state by changing the volume or the number of moles of the different species.

Note that we can also derive a relationship between A and the canonical partition function $Q(\{n\},V,T)$ from the Legendre transform relation $A = E - TS$. Since

$$E = -\frac{\partial \ln Q}{\partial \beta} \tag{1.9.34}$$

and

$$TS = -T\frac{\partial A}{\partial T} = \beta\frac{\partial A}{\partial \beta} \tag{1.9.35}$$

we see that

$$A = -\frac{\partial \ln Q}{\partial \beta} - \beta\frac{\partial A}{\partial \beta} \tag{1.9.36}$$

This simple differential equation for A has the solution

$$A(\{n\},V,T) = -\frac{1}{\beta}\ln Q(\{n\},V,T) \tag{1.9.37}$$

which can be verified simply by substituting this solution back into the equation and showing that the equation is satisfied.

Transforming to the Isothermal-Isobaric Ensemble

The isothermal-isobaric ensemble uses $\{n\}$, P, and T as the control variables. Thus, this ensemble results from performing a Legendre transform of the Helmholtz free energy from volume V to pressure P. The volume in the Helmholtz free energy $A(\{n\},V,T)$ is transformed into the external pressure P yielding a new free energy denoted $\tilde{A}(\{n\},P,T)$:

$$\tilde{A}(\{n\},P,T) = A(\{n\},V(\{n\},P,T),T) - V(\{n\},P,T)\frac{\partial A}{\partial V} \tag{1.9.38}$$

Using the fact that $P = -\partial A/\partial V$, we obtain

$$\tilde{A}(\{n\},P,T) = A(\{n\},V(\{n\},P,T),T) + PV(\{n\},P,T) \tag{1.9.39}$$

The function $\tilde{A}(\{n\},P,T)$ is known as the *Gibbs free energy* and is denoted $G(\{n\},P,T)$. Since G is a function of $\{n\}$, p, and T, a small change in each of these control variables yields a change in G given by

$$dG = \sum_{k=1}^{M}\left(\frac{\partial G}{\partial n_k}\right)_{P,T} dn_k + \left(\frac{\partial G}{\partial P}\right)_{\{n\},T} dP + \left(\frac{\partial G}{\partial T}\right)_{\{n\},P} dT \tag{1.9.40}$$

However, since $G = A + PV$, the differential change dG can also be expressed as

$$dG = dA + P\,dV + V\,dP \tag{1.9.41}$$

$$= -P\,dV + \sum_{k=1}^{M}\mu_k\,dn_k - S\,dT + P\,dV + V\,dP \tag{1.9.42}$$

$$= \sum_{k=1}^{M}\mu_k\,dn_k + V\,dP - S\,dT \tag{1.9.43}$$

where the second line follows from Equation 10.26. Thus, equating Equation 10.36 with Equation 10.35, the thermodynamic relations of the isothermal-isobaric ensemble follow:

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{P,T}, \quad \langle V\rangle = \left(\frac{\partial G}{\partial P}\right)_{\{n\},T}, \quad S = -\left(\frac{\partial G}{\partial T}\right)_{\{n\},P} \tag{1.9.44}$$

As before, the volume in Equation 10.37 must be regarded as an average over instantaneous volume fluctuations.

Since $G = A + PV = E - TS + PV = (E + PV) - TS$, $G = H - TS$, where H is the enthalpy. We can also derive a relationship between G and the canonical partition function $\Delta(\{n\},P,T)$ from the Legendre transform relation $G = H - TS$. Since

$$H = -\frac{\partial \ln \Delta}{\partial \beta} \tag{1.9.45}$$

and

$$TS = -T\frac{\partial G}{\partial T} = \beta\frac{\partial G}{\partial \beta} \tag{1.9.46}$$

we see that

$$G = -\frac{\partial \ln \Delta}{\partial \beta} - \beta\frac{\partial G}{\partial \beta} \tag{1.9.47}$$

This simple differential equation for A has the solution

$$G(\{n\},P,T) = -\frac{1}{\beta}\ln \Delta(\{n\},P,T) \tag{1.9.48}$$

which can be verified simply by substituting this solution back into the equation and showing that the equation is satisfied.

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1.10: Physical significance of free energy, Euler's theorem, Maxwell relations

Physical and Chemical Relevance of Free Energy

In this section, we will consider some examples showing the significance of free energies.

Drug binding

In pharmaceutical chemistry, free energies play a critical role in quantifying the strength of binding between an enzyme and an inhibitor such as a small-molecule inhibitor. An example of this is the use of the HIV-1 protease as a target for anti-AIDS therapies. The HIV-1 protease is a critical enzyme for the replication cycle of the AIDS virus, and numerous small-molecule inhibitors exist for arresting its catalytic function. An example is shown in the figure below: In designing such inhibitors, the binding process, itself, illustrated in the cartoon below is critical. This process

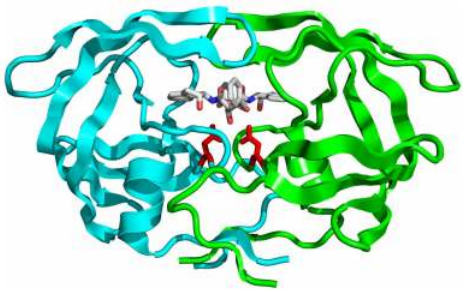


Figure 11.1: Illustration of a small molecule inhibitor complexed with the HIV-1 protease.

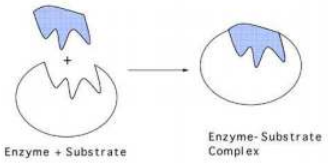


Figure 11.2: Cartoon illustrating the drug-enzyme binding process.

is an equilibrium between enzyme E, inhibitor I, and the bound complex EI:

$$EI \leftrightharpoons E + I \tag{1.10.1}$$

The equilibrium constant for this process

$$K = \frac{[E][I]}{[EI]} \equiv K_i \tag{1.10.2}$$

is known as the *inhibition constant*. The smaller the value of K_i, the greater the concentration of bound complexes, hence, the greater the strength of the binding. Optimal inhibitors of an enzyme have nanomolar or smaller K_i values. In general, the equilibrium constant for a process is determined by the change in the Gibbs free energy of the process. Hence, K_i is determined by the binding free energy process

$$\Delta G_{\text{bind}} = \Delta G(EI) - \Delta G(E) - \Delta G(I) \tag{1.10.3}$$

so that

$$K_i = e^{\beta \Delta G_{\text{bind}}} \tag{1.10.4}$$

Solvation free energies

As the previous example showed, the binding free energy quantifies the strength of the interaction between a drug and a target enzyme. While this is a critical component of the drug design process, another process of key importance is solubility. Most medications are formulated as tablets or gel capsules, both of which contain small crystalline particles. These crystalline particles must be water soluble in order for them to be bioavailable. The solvation process for a substance A is captured in the reaction

$$A(g) \leftrightharpoons A(aq) \tag{1.10.5}$$

and illustrated humorously below: The equilibrium constant for this process K_{solv} is also determined by the solvation



Figure 11.3: Illustration of the solvation process.

Gibbs free energy ΔG_{solv}:

$$K_{solv} = e^{-\beta \Delta G_{solv}} \tag{1.10.6}$$

As an example of calculation of ΔG_{solv} and ΔA_{solv}, the plot below shows a computer simulation of the solvation of methane in water, in which solvated configurations are sampling via molecular dynamics (numerical solution of Newton's equations of motion), and an algorithm designed to speed the convergence with simulation time of the free energy is employed. The convergence of ΔA_{solv} is compared to experiment and known theoretical values of ΔG_{solv}. In this case, it can be seen that ΔG_{solv} and ΔA_{solv} are nearly identical.

Configurational Free Energies

Free energies can be used to characterize the conformational preferences and the conformational equilibria of complex molecules. Such free energies can be useful, for example, in understanding the process of protein or polypeptide folding. An example of the folding of an alanine decamer into an alpha-helix is shown below. The folding process can be characterized in terms of a particular mechanical coordinate in the system known as a *reaction coordinate*, and the free energy along such a coordinate can be mapped out in order to obtain free energy differences between

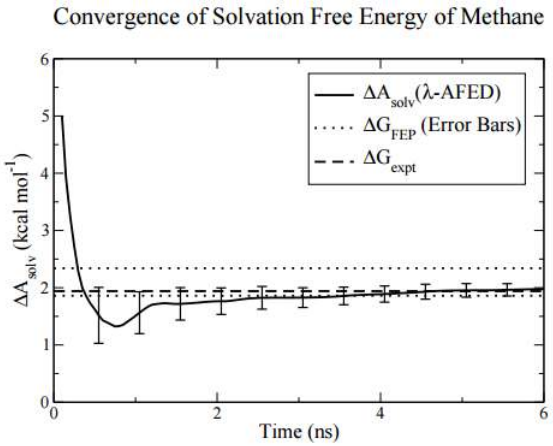


Figure 11.4: Convergence of a calculation of ΔA_{solv} for methane in water and comparison to the experimental value.

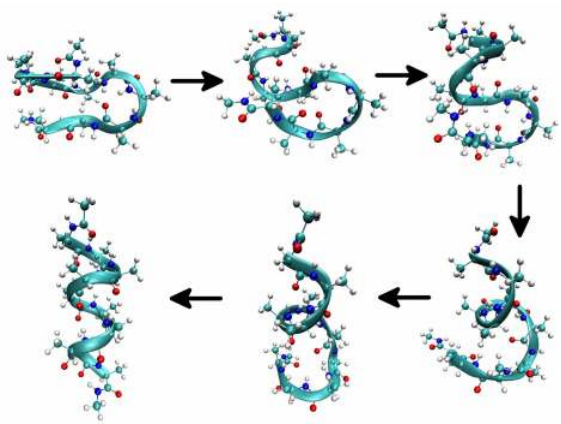


Figure 11.5: Folding pathway of an alanine decamer.

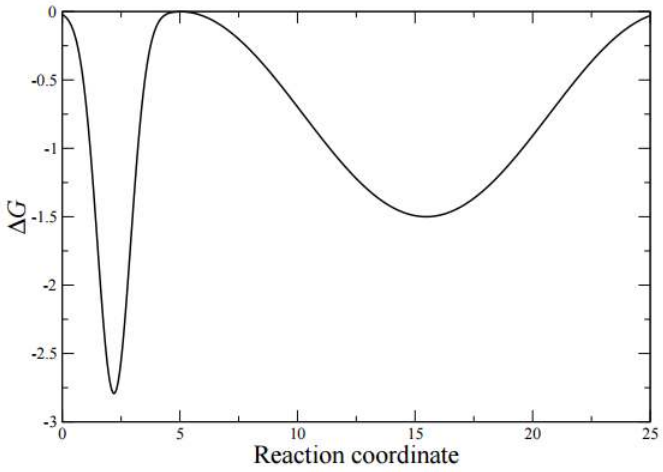


Figure 11.6: Typical folding free energy curve.

unfolded, partially folded, and fully folded conformations. For folding, a useful coordinate is the root-mean square deviation (RMSD) from the fully folded state of the alpha carbons along the peptide backbone. A typical free energy map of this type appears as in the figure below. The free energy curve shows a narrow and deep minimum at small values of the reaction coordinate, here the RMSD from the folded conformation. This deep minimum is associated with the folded state. The wide basin at large values of the RMSD corresponds to metastable intermediates, which are misfolded states and β-hairpin type conformations.

Free Energies of Crystalline Polymorphs

Polymorphism refers to the ability of certain small organic molecules to form numerous distinct crystal structures. This is a critical problem in the pharmaceutical industry, where most medications are administered in crystalline form. Hence, if a particular compound is able to convert from a metastable, soluble crystal to a highly stable, insoluble form, while the medication sits on the shelf, is a serious problem that can lead to expensive recalls. A *priori* prediction of crystalline polymorphs of small molecules is, therefore, a problem of critical importance. Computational prediction of polymorphs can play an important role in this endeavor, and the development of such techniques is an outstanding grand challenge problem. A successful prediction of polymorphs should also include a thermodynamic ranking of these structures, and such a ranking should be based on the relative free energy of the polymorphs. An example of the polymorphs of benzene at $\mathbf{100}$ K and $\mathbf{2}$ GPa pressure is shown in the figure below along with the unit cells of each crystal structure. The figure shows free energies (green curve), simple lattice energies at $\mathbf{0}$ K (red curve), and

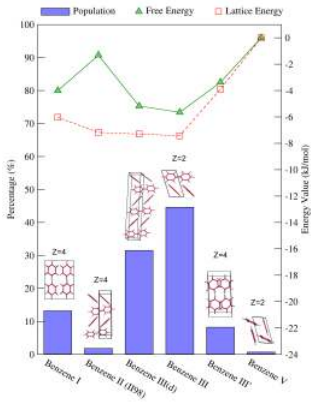


Figure 11.7: Relative free energies of the polymorphs of solid benzene.

the relative populations of different polymorphs (blue bars). The figure suggests that the Benzene III polymorph is thermodynamically the most stable structure under the conditions reported above.

Euler's Theorem

Recall the definition of the Helmholtz free energy is $\boldsymbol{A = E - TS}$, hence, a change in $\boldsymbol{A}$ at constant temperature is

$$\Delta A = \Delta E - T\Delta S \tag{1.10.7}$$

Since $T\Delta S = \Delta Q_{\text{rev}}$, we obtain

$$\Delta A = \Delta E - \Delta Q_{\text{rev}} \tag{1.10.8}$$

which means that

$$\Delta A = \Delta W_{\text{rev}} \tag{1.10.9}$$

Hence, the change in the Helmholtz free energy in an isothermal process is equal to the reversible work performed on the system in the process.

There is another way to obtain this relation that involves a very general property of many thermodynamic functions. This property is a consequence of a theorem known as *Euler's Theorem*. Euler's theorem is a general statement about a certain class of functions known as *homogeneous functions of degree* n. Consider a function $f(x_1, \dots, x_N)$ of N variables that satisfies

$$f(\lambda x_1, \dots, \lambda x_k, x_{k+1}, \dots, x_N) = \lambda^n f(x_1, \dots, x_k, x_{k+1}, \dots, x_N) \tag{1.10.10}$$

for an arbitrary parameter, λ. We call such a function a *homogeneous function of degree* n in the variables $x_1, \dots, x_k$. The function $f(x) = x^2$, for example, is a homogeneous function of degree 2. The function $f(x, y, z) = xy^2 + z^3$ is a homogeneous function of degree 3 in all three variables x, y, and z. The function $f(x, y, z) = x^2(y^2 + z)$ is a homogeneous function of degree 2 in x but not in y and z. The function $f(x, y) = e^{xy} - xy$ is not a homogeneous function in either x or y.

Euler's theorem states the following: Let $f(x_1, \dots, x_N)$ be a homogeneous function of degree n in x_1, x_k. Then,

$$nf(x_1, \dots, x_N) = \sum_{i=1}^{k} x_i \frac{\partial f}{\partial x_i} \tag{1.10.11}$$

The proof of Euler's theorem is straightforward. Beginning with Equation 11.10, we differentiate both sides with respect to λ to yield:

$$\frac{d}{d\lambda} f(\lambda x_1, \dots, \lambda x_k, x_{k+1}, \dots, x_N) = \frac{d}{d\lambda} \lambda^n f(x_1, \dots, x_k, x_{k+1}, \dots, x_N) \tag{1.10.12}$$

$$\sum_{i=1}^{k} x_i \frac{\partial f}{\partial (\lambda x_i)} = n\lambda^{n-1} f(x_1, \dots, x_k, x_{k+1}, \dots, x_N) \tag{1.10.13}$$

Since λ is arbitrary, we may freely choose $\lambda = 1$, which yields

$$\sum_{i=1}^{k} x_i \frac{\partial f}{\partial x_i} = nf(x_1, \dots, x_k, x_{k+1}, \dots, x_N) \tag{1.10.14}$$

and proves the theorem.

What does Euler's theorem have to do with thermodynamics? Consider, for example, the Helmholtz free energy $A(N, V, T)$, which depends on two extensive variables, N and V. Since A is, itself, extensive, $A \sim N$, and since $V \sim N$, A must be a homogeneous function of degree 1 in N and V, i.e. $A(\lambda N, \lambda V, T) = \lambda A(N, V, T)$. Applying Euler's theorem, it follows that

$$A(N, V, T) = V \frac{\partial A}{\partial V} + N \frac{\partial A}{\partial N} \tag{1.10.15}$$

From the thermodynamic relations of the canonical ensemble for pressure and chemical potential, we have $P = -(\partial A/\partial V)$ and $\mu = (\partial A/\partial N)$. Thus,

$$A = -PV + \mu N \tag{1.10.16}$$

We can verify this result by recalling that

$$A(N, V, T) = E - TS \tag{1.10.17}$$

From the first law of thermodynamics,

$$E - TS = -PV + \mu N \tag{1.10.18}$$

so that

$$A(N,V,T) = -PV + \mu N \tag{1.10.19}$$

which agrees with Euler's theorem. Now, a small change in A under reversible conditions gives

$$dA = -P(V)\,dV + \mu(N)\,dN \tag{1.10.20}$$

which is a general expression for the reversible work done on a system when both volume and number of particles (or moles) changes. In fact, any extensive thermodynamic quantity must be a homogeneous function of degree 1 in its extensive arguments.

Thus, the Gibbs free energy $G(N,P,T)$ is a homogeneous function of degree 1 in N. Hence, we can write

$$G = N\frac{\partial G}{\partial N} = \mu N \tag{1.10.21}$$

Thus, $dG = \mu(N)\,dN$, and the quantity $dG + P\,dV = G + P_{ext}\,dV$ is the reversible work performed on a system under isobaric conditions.

Maxwell Relations

Free energies provide a route to relating changes in thermodynamic derivatives, i.e., changes in certain thermodynamic quantities under different conditions. These useful relations are not always obvious but can be easily derived starting from either a Helmholtz or Gibbs free energy. Unlike the relations of the previous section, the relations we will consider next emerge from second derivatives of the free energy functions and are referred to as *Maxwell relations* after the 19th Century Scottish physicist James Clerk Maxwell, who also developed the classical theory of electromagnetic fields (in the form of the celebrated Maxwell equations). We will see that the first derivative relations of the previous section, however, provide the starting point.

Consider the Helmholtz free energy $A = E - TS$. In a process that changes temperature and energy (and, therefore, the entropy as well), the free energy change is

$$dA = dE - S\,dT - T\,dS \tag{1.10.22}$$

From the first law, $dE = -P\,dV + T\,dS$, hence

$$dA = -P\,dV + T\,dS - S\,dT - T\,dS = -P\,dV - S\,dT \tag{1.10.23}$$

However, by the chain rule, if N remains fixed

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \tag{1.10.24}$$

Equating these two relations, we find

$$P = -\left(\frac{\partial A}{\partial V}\right)_T, \quad S = -\left(\frac{\partial A}{\partial T}\right)_V \tag{1.10.25}$$

It is trivially obvious that

$$\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V} \tag{1.10.26}$$

However, the above relation tells us that

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{1.10.27}$$

which is an example of a Maxwell relation. It tells us how to compute the change in entropy with respect to volume from a knowledge of the equation of state. If we integrate both sides, the entropy change when the volume changes from V_1 to V_2 is

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV \tag{1.10.28}$$

Thus, for an ideal gas, $P = nRT/V$, $\partial P/\partial T = nR/V$, hence,

$$\Delta S = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \left(\frac{V_2}{V_1} \right) \tag{1.10.29}$$

If N is allowed to change as well, then the Equations 11.22 and 11.23 must be modified to read

$$dA = -P\, dV + \mu\, dN - S\, dT \tag{1.10.30}$$

$$dA = \left(\frac{\partial A}{\partial N} \right)_{V,T} dN \left(\frac{\partial A}{\partial V} \right)_{N,T} dV + \left(\frac{\partial A}{\partial T} \right)_{N,V} dT \tag{1.10.31}$$

so that

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T} \tag{1.10.32}$$

Think about the additional Maxwell relations that can be derived from this relation for the chemical potential.

If we start with the Gibbs free energy instead, and consider the second derivative of G with respect to N and P under isothermal conditions, we obtain another useful Maxwell relation

$$\frac{\partial^G}{\partial N \partial P} = \frac{\partial^2 G}{\partial P \partial N} \tag{1.10.33}$$

$$\frac{\partial \mu}{\partial P} = \frac{\partial \langle V \rangle}{\partial N} \tag{1.10.34}$$

which tells us that the change in chemical pressure with respect to pressure is equal to the change in the average volume with respect to the number of particles or the number of moles.

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1.11: Carnot engines, thermodynamic entropy, and the second and third laws

Carnot Engines and the Thermodynamic Definition of Entropy

We have been using two definitions of the entropy almost interchangeable. One is a purely thermodynamic definition involving the heat absorbed by a system in a reversible process at temperature T :

$$\Delta S = \int_A^B \frac{dQ_{\text{rev}}}{T} \tag{1.11.1}$$

while the other is purely statistical. Given two states A and B with numbers of microstates Ω_A and Ω_B, the change in entropy is determined from Boltzmann's relation:

$$\Delta S = S_B - S_A = k_B \ln \Omega_B - k_B \ln \Omega_A = k_B \ln \left(\frac{\Omega_B}{\Omega_A} \right) \tag{1.11.2}$$

Two questions then naturally arise. Where does the thermodynamic definition actually come from, and are these two definitions really equivalent? In order to explore this, we will study a particular thermodynamic cycle called an *engine*.

In general, the processes that engines undergo are highly irreversible. As an idealization, we will consider the operation of a particular kind of engine, called a *Carnot* engine, that operates reversibly between its initial, intermediate and final states. By analyzing such a device, it should be possible to place an upper bound on the efficiency of any engine operating between a high temperature reservoir at T_h and a low temperature reservoir at T_l.

Consider the thermodynamic path shown below:

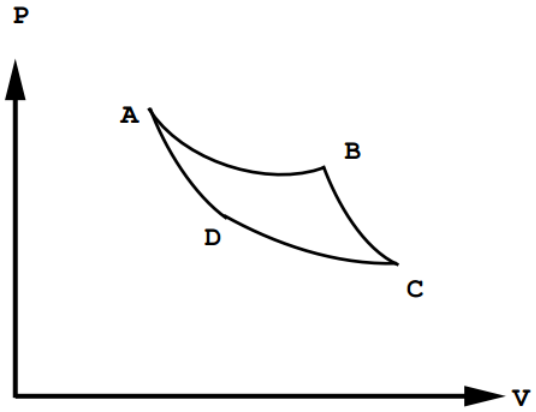


Figure 12.1: *The Carnot cycle.*

This closed thermodynamic path or *cycle* is called the *Carnot cycle*. In the ABC portion of the cycle, the system expands, so it does work. In the CDA portion of the path, the system is compressed, so work is done on it. The net work, which is the sum of contributions from paths ABC and path CDA, is the net work done by the system, so it must be negative:

$$W_{\text{net}} = -\int_{\text{path } ABC} P\, dV - \int_{\text{path } CDA} P\, dV \tag{1.11.3}$$

Note that the net work performed by the engine is just the area of enclosed by the by four paths in the $P-V$ plane. Since, for a closed path, the change in energy is 0, the net work done by the gas must be equal the negative of the heat absorbed by the system:

$$W = -W_{\text{net}} = -q \tag{1.11.4}$$

Now suppose that the system is an ideal gas. We have already developed expressions for the work done by/on the the system for various parts of this thermodynamic cycle:

- **Path AB: Isothermal expansion at temperature T_h:**

$$W_{AB} = -q_{AB} = -nRT_h \ln \left(\frac{V_B}{V_A} \right) \tag{1.11.5}$$

- **Path BC: Adiabatic expansion:**

$$\begin{aligned} q_{BC} &= 0 \\ W_{BC} &= nc_V(T_l - T_h) \end{aligned} \tag{1.11.6}$$

- **Path CD: Isotherm compression at temperature T_l:**

$$W_{CD} = -q_{CD} = -nRT_l \ln\left(\frac{V_D}{V_C}\right) \tag{1.11.7}$$

- **Path DA: Adiabatic compression:**

$$\begin{aligned} q_{DA} &= 0 \\ W_{DA} &= nc_V(T_h - T_l) \end{aligned} \tag{1.11.8}$$

The net work done on the system is

$$W_{\text{net}} = W_{AB} + W_{BC} + W_{CD} + W_{DA} \tag{1.11.9}$$

$$= -nRT_h \ln\left(\frac{V_B}{V_A}\right) + nRT_l \ln\left(\frac{V_C}{V_D}\right) \tag{1.11.10}$$

Recall, however, that in an adiabatic expansion, the temperatures T_1 and T_2 are related to the volumes V_1 and V_2 by

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \tag{1.11.11}$$

which can be applied to the paths BC and DA, the adiabatic expansion and compression parts of the cycle. Thus, for the path BC,

$$\frac{T_h}{T_l} = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \tag{1.11.12}$$

and for the path DA,

$$\frac{T_h}{T_l} = \left(\frac{V_D}{V_A}\right)^{\gamma-1} \tag{1.11.13}$$

from which it follows that

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \tag{1.11.14}$$

or

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \tag{1.11.15}$$

and the net work done on the system is

$$W_{\text{net}} = -nR(T_h - T_l) \ln\left(\frac{V_B}{V_A}\right) \tag{1.11.16}$$

Note also that, since a complete cycle has been made, $\Delta E = 0$ for the cycle. Thus, from the first law of thermodynamics,

$$-W_{\text{net}} = q_{AB} + q_{CD} \tag{1.11.17}$$

which is the net heat absorbed by the system. Since heat is only absorbed/discharged during the isothermal parts of the cycle, only q_{AB} and q_{CD} are nonzero.

In the first part of the next lecture, the derivation will continue, beginning with a determination of the maximum efficiency of a Carnot engine.

The efficiency of a device is defined to be the net work it can produce per unit of heat taken in:

$$\epsilon = -\frac{W_{\text{net}}}{q_{AB}} \tag{1.11.18}$$

Thus, if all of the heat taken in is converted to useful work with no discharge of waste heat, then the device is 100% efficient. We will now show that such a case is not possible.

For the Carnot cycle, in which a system containing an ideal gas undergoes reversible transformations around the cycle, we have

$$W_{\text{net}} = -nR(T_h - T_l)\ln\left(\frac{V_B}{V_A}\right) \tag{1.11.19}$$

$$q_{AB} = nRT_h \ln\left(\frac{V_B}{V_A}\right) \tag{1.11.20}$$

And the negative ratio of these, which gives the efficiency, is

$$\epsilon = \frac{nR(T_h - T_l)\ln(V_B/V_A)}{nRT_h \ln(V_B/V_A)} = \frac{T_h - T_l}{T_h} = 1 - \frac{T_l}{T_h} \tag{1.11.21}$$

Thus, for an engine operating reversibly between a high temperature T_h and a low temperature T_l, the maximum efficiency of such a machine is $1 - (T_l/T_h)$. In order to achieve, 100% efficiency, therefore, it would be necessary to make $T_l = 0$ or $T_h = \infty$, neither of which is possible. However, the larger the temperature difference, the greater will be the efficiency of the device. The difficulty with large temperature differences, in general, is that they are difficult to make, and it is also difficult to find materials that can withstand both extremely high AND extremely low temperatures.

Although this result was derived for a system containing an ideal gas, it turns out to be true for *all* Carnot engines operating reversibly between T_h and T_l. To prove this result, the technique of proof by contradiction will be used.

Assume that there are two engines operating reversibly between T_h and T_l with different efficiencies, ϵ_1 and ϵ_2 such that $\epsilon_1 > \epsilon_2$. The machines are adjusted so that work output of both is equal, $-W_1 = -W_2$. We let the more efficient machine, 1, be operated as a normal Carnot engine, withdrawing heat at T_h, discarding waste heat at T_l and producing an output $-W_1$ of useful work. The less efficient engine is run in reverse, as a "heat pump," withdrawing heat at the low temperature T_l, consuming useful work from an outside source, and delivering a quantity of heat to the high temperature T_h. This is how a refrigerator operates. In this case, the work output of machine 1 is used to operate machine 2. The figure below illustrates this:

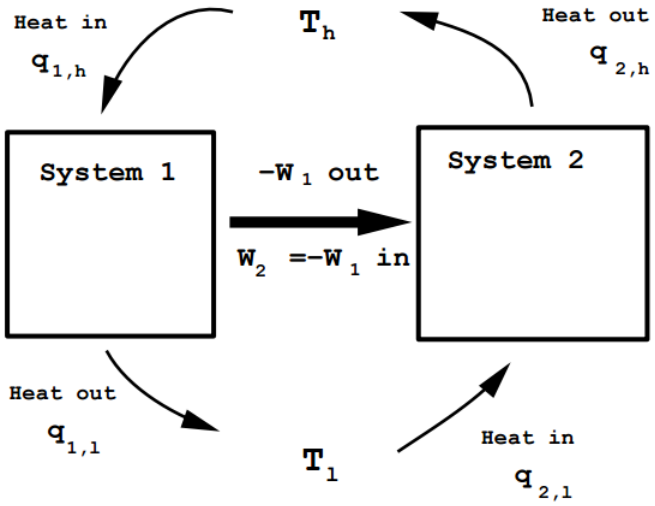


Figure 12.2: *Illustrating the Carnot engine.*

Since $-W_1 = W_2$, the net work output of the two machines combined is $W_{\text{tot}} = 0$. Also, since each machine completes a thermodynamic cycle, the total energy change of the two machines combined is also 0 ($\Delta E_{\text{tot}} = 0$). Since $\epsilon_1 > \epsilon_2$,

$$\frac{-W_1}{q_{1,h}} > \frac{W_2}{-q_{2,h}} \tag{1.11.22}$$

$$-W_1 = W_2 \tag{1.11.23}$$

$$\Rightarrow \frac{1}{q_{1,h}} > \frac{1}{q_{2,h}} \tag{1.11.24}$$

$$q_{1,h} < q_{2,h} \tag{1.11.25}$$

But from the first law of thermodynamics, since $\Delta E_{\text{tot}} = 0$ and $W_{\text{tot}} = 0$, the total heat absorbed by the system $q_{\text{tot}} = 0$. The total heat absorbed is

$$q_{1,h} - q_{1,l} + q_{2,l} - q_{2,h} = 0 \tag{1.11.26}$$

Thus,

$$q_{1,h} - q_{2,h} = q_{1,l} - q_{2,l} \tag{1.11.27}$$

The left side is the net heat absorbed at T_h and the right side is the net heat discharged at T_l. Since $q_{1,h} < q_{2,h}$, the left side is negative, and so the right side must be negative as well, and

$$q_{1,l} < q_{2,l} \tag{1.11.28}$$

Since $q_{2,h} > q_{1,h}$ there is a net amount of heat delivered to the high temperature reservoir, and a net amount of heat extracted from the low temperature reservoir. In other words, the combined machine is capable of extracting an amount of heat from a cold source and delivering it to a hot source with **NO** expenditure of work!!!!!

While there is no logical contradiction here, the result would seem to imply that it must be possible for heat to flow from cold to hot without input of work, which has never been observed. Rather, only the opposite has been observed, heat flowing naturally from hot to cold. Thus, we are lead to conclude that all Carnot engines must have the same efficiency.

Derivation of the Thermodynamic Definition of Entropy

We saw in the analysis above that, for a Carnot cycle:

$$-W_{\text{net}} = q_h + q_l \tag{1.11.29}$$

Thus, the efficiency can be expressed as

$$\epsilon = \frac{-W_{\text{net}}}{q_h} = \frac{q_h + q_l}{q_h} = \frac{T_h - T_l}{T_h} \tag{1.11.30}$$

which implies that

$$1 + \frac{q_l}{q_h} = 1 - \frac{T_l}{T_h} \tag{1.11.31}$$

or

$$\frac{q_l}{q_h} = -\frac{T_l}{T_h} \tag{1.11.32}$$

$$\frac{q_l}{T_l} = -\frac{q_h}{T_h} \tag{1.11.33}$$

$$\frac{q_l}{T_l} + \frac{q_h}{T_h} = 0 \tag{1.11.34}$$

Recall that a state function is a thermodynamic quantity, whose change between initial and final states is independent of the path between the states. By extension, it follows that a state function is one whose change around any *closed* thermodynamic path is 0. Thus, since q/T is zero for the Carnot cycle, it would seem that q/T is a state function. In fact, this turns out to be true. To see this, note that any Carnot cycle can be composed of an infinite number of Carnot cycles for which the isothermal parts of the cycle are of infinitesimally small length (see Figure 8.6 in the text). The quantity of heat absorbed along each of these isotherms is δq_i for the i^{th} cycle. Since $\delta q_{i,h}/T_{i,h} + \delta q_{i,l}/T_{i,l} = 0$ for the i^{th} cycle, summing over all cycles gives

$$\sum_i \left[\frac{\delta q_{i,h}}{T_{i,h}} + \frac{\delta q_{i,l}}{T_{i,l}} \right] = 0 \tag{1.11.35}$$

which approaches the integral expression as the number of cycles becomes infinitely large:

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \tag{1.11.36}$$

where $\oint$ indicates that the integral is taken over a *closed* thermodynamic cycle. This, then, leads to the Clausius definition entropy, as the state function, $\Delta S = S_f - S_i$, given by

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} \tag{1.11.37}$$

Clearly, then $\Delta S = 0$ over any closed path. In the next section, we will show that this definition of ΔS is consistent with the statistical (Boltzmann) definition for an ideal gas.

Isothermal Processes in an Ideal Gas

In an isothermal process, the temperature is held constant so that

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} = \frac{1}{T}\int_i^f dq_{\text{rev}} \tag{1.11.38}$$

The differential dq_{rev} can be integrated as a perfect differential q_{rev}, which is the heat absorbed by the system in the *reversible* process that takes the system from state i to state f:

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{1.11.39}$$

Isothermal expansion/compression of an ideal gas

In the last chapter, we derived the expression for the isothermal expansion/compression of an ideal gas from a volume V_1 to a volume V_2:

$$q_{\text{rev}} = nRT \ln\left(\frac{V_2}{V_1}\right) \tag{1.11.40}$$

From this, it follows that the entropy change in the expansion/compression is

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) \tag{1.11.41}$$

To see that the same expression results from the Boltzmann definition of entropy, recall that the number of microscopic states is

$$\Omega(N,V,T) = cV^N(k_BT)^{3N/2} \tag{1.11.42}$$

At constant temperature, the number of microscopic states available to the system in the volume V_1 and in the volume V_2 are, respectively,

$$\begin{aligned} \Omega_1 &= cV_1^N(k_BT)^{3N/2} \\ \Omega_2 &= cV_2^N(k_BT)^{3N/2} \end{aligned} \tag{1.11.43}$$

Thus,

$$\Delta S = k_B \ln\left(\frac{\Omega_2}{\Omega_1}\right) \tag{1.11.44}$$

$$= k_B \ln\left(\frac{V_2}{V_1}\right)^N \tag{1.11.45}$$

$$= Nk_B \ln\left(\frac{V_2}{V_1}\right) \tag{1.11.46}$$

$$= nR \ln\left(\frac{V_2}{V_1}\right) \tag{1.11.47}$$

which agrees with the thermodynamic definition perfectly.

Isochoric heat absorption/emission of an ideal gas

An *isochoric* process is one that occurs at constant volume. Consider the heat absorption/emission of an ideal gas at constant volume. A small amount of heat dq_{rev} absorbed a change in temperature dT related to the heat dq_{rev} by

$$dq_{\text{rev}} = nc_V dT \tag{1.11.48}$$

Thus, the entropy change when the temperature goes from T_1 to T_2 is

$$\Delta S = \int_{T_1}^{T_2} \frac{nc_V dT}{T} \tag{1.11.49}$$

$$= nc_V \ln\left(\frac{T_2}{T_1}\right) \tag{1.11.50}$$

From the Boltzmann definition, the number of microstates at temperatures T_1 and T_2 and volume V are, respectively,

$$\begin{aligned} \Omega_1 &= cV^N (k_B T_1)^{3N/2} \\ \Omega_2 &= cV^N (k_B T_2)^{3N/2} \end{aligned} \tag{1.11.51}$$

so that

$$\Delta S = k_B \ln\left(\frac{\Omega_2}{\Omega_1}\right) \tag{1.11.52}$$

$$= k_B \ln\left(\frac{T_2}{T_1}\right)^{3N/2} \tag{1.11.53}$$

$$= \frac{3}{2} N k_B \ln\left(\frac{T_2}{T_1}\right) \tag{1.11.54}$$

$$= \frac{3}{2} nR \ln\left(\frac{T_2}{T_1}\right) \tag{1.11.55}$$

Recalling that c_V for an ideal gas is

$$c_V = \frac{3}{2} R \tag{1.11.56}$$

gives

$$\Delta S = nc_V \ln\left(\frac{T_2}{T_1}\right) \tag{1.11.57}$$

which, again, agrees with the thermodynamic definition.

Isobaric heat absorption/emission of an ideal gas

By analogy with the isochoric process, the entropy change in an isobaric process can be shown to be

$$\Delta S = nc_P \ln\left(\frac{T_2}{T_1}\right) \tag{1.11.58}$$

In order to derive this from the Boltzmann definition, we need to express the number of microstates of an ideal gas at constant pressure. At constant volume, we have

$$\Omega(N, V, T) = cV^N (k_B T)^{3N/2} \tag{1.11.59}$$

However, from the ideal gas law:

$$V = \frac{N k_B T}{P} \tag{1.11.60}$$

Thus, the number of microstates becomes

$$\Omega(N, P, T) = CP^{-N} (k_B T)^{5N/2} \tag{1.11.61}$$

where C is another constant. Thus, at constant pressure P and temperatures T_1 and T_2, the respective numbers of microstates are

$$\begin{aligned} \Omega_1 &= CP^{-N} (k_B T_1)^{5N/2} \\ \Omega_2 &= CP^{-N} (k_B T_2)^{5N/2} \end{aligned} \tag{1.11.62}$$

Thus, the entropy change is

$$\Delta S = k_B \ln \left(\frac{T_2}{T_1}\right)^{5N/2} \tag{1.11.63}$$

$$= \frac{5}{2} N k_B \ln \left(\frac{T_2}{T_1}\right) \tag{1.11.64}$$

$$= \frac{5}{2} nR \ln \left(\frac{T_2}{T_1}\right) \tag{1.11.65}$$

However, recognizing that $5R/2$ is just the constant pressure heat capacity c_P, we have

$$\Delta S = nc_P \ln \left(\frac{T_2}{T_1}\right) \tag{1.11.66}$$

which, again, agrees with the thermodynamic definition.

Adiabatic expansion/compression of an ideal gas

Recall that in an adiabatic expansion/compression, no heat is absorbed or emitted. Hence, $dq_{\text{rev}} = 0$ and $\Delta S = 0$. In order to derive this result from the Boltzmann definition, we note that P, V, and T all change in the adiabatic process, hence,

$$\begin{aligned} \Omega_1 &= cV_1^N (k_B T_1)^{3N/2} \\ \Omega_2 &= cV_2^N (k_B T_2)^{3N/2} \end{aligned} \tag{1.11.67}$$

The ratio is

$$\frac{\Omega_2}{\Omega_1} = \frac{V_2^N (k_B T_2)^{3N/2}}{V_1^N (k_B T_1)^{3N/2}} = \left[\frac{V_2}{V_1} \frac{T_2^{3/2}}{T_1^{3/2}}\right] \tag{1.11.68}$$

However, in an adiabatic process, we showed that the temperatures and volumes are related by

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \tag{1.11.69}$$

where $\gamma = 5/3$ for an ideal gas. This implies that

$$T_1 V_1^{2/3} = T_2 V_2^{2/3} \tag{1.11.70}$$

$$T_1^{3/2} V_1 = T_2^{3/2} V_2 \tag{1.11.71}$$

$$1 = \frac{T_2^{3/2}}{T_1^{3/2}} \frac{V_2}{V_1} \tag{1.11.72}$$

which is just the ratio Ω_2/Ω_1. Therefore, from the Boltzmann definition:

$$\Delta S = k_B \ln \left(\frac{\Omega_2}{\Omega_1}\right) = k_B \ln (1) = 0 \tag{1.11.73}$$

The Second and Third Laws of Thermodynamics

We noted that entropy is a thermodynamic state function related to the number of microscopic states available to a system. Thus, any process that gives rise to an increase in the number of microscopic states in a system will also lead to an increase in the entropy. In order to quantify this, let us consider another simple thought experiment.

Consider the irreversible, isothermal expansion of an ideal gas. This can be achieved by allowing the external pressure P_{ext} to drop suddenly below the internal pressure $P^{(\text{int})}$. The work done on the gas in the expansion is

$$W_{\text{irrev}} = -\int P_{\text{ext}} dV \tag{1.11.74}$$

If we compare such a process to a *reversible* expansion in which the gas is always in equilibrium with its surroundings, then $P^{(\text{int})} \approx P_{\text{ext}}$, and

$$W_{\text{rev}} = -\int P^{(\text{int})} dV \tag{1.11.75}$$

In the irreversible process, since P_{ext} drops quickly, $P_{\text{ext}} < P^{(\text{int})}$ and hence,

$$\begin{aligned} -W_{\text{irrev}} &< -W_{\text{rev}} \\ W_{\text{irrev}} &> W_{\text{rev}} \end{aligned} \tag{1.11.76}$$

Now let Q_{rev} and Q_{irrev} be the amounts of heat absorbed by the gas in the reversible and irreversible processes, respectively. Since energy is a state function, the first law tells us that the change in energy can be computed along the reversible or irreversible path with the same result:

$$\Delta E = Q_{\text{rev}} + W_{\text{rev}} = Q_{\text{irrev}} + W_{\text{irrev}} \tag{1.11.77}$$

Since $W_{\text{irrev}} > W_{\text{rev}}$, it must follow that $Q_{\text{irrev}} < Q_{\text{rev}}$. Thus, for small changes, $dQ_{\text{irrev}} < dQ_{\text{rev}}$. Therefore, in an isothermal process

$$\frac{dQ_{\text{irrev}}}{T} < \frac{dQ_{\text{rev}}}{T} \tag{1.11.78}$$

Since

$$dS = \frac{dQ_{\text{rev}}}{T} \tag{1.11.79}$$

it follows that

$$dS > \frac{dQ_{\text{irrev}}}{T} \tag{1.11.80}$$

Generally,

$$dS \geq \frac{dQ}{T} \tag{1.11.81}$$

or

$$\Delta S \geq \int \frac{dQ}{T} \tag{1.11.82}$$

where equality holds *only* for reversible processes. This inequality is called the *Clausius inequality*.

Now, we apply the Clausius inequality to the entire thermodynamic universe (system + surroundings). Since the universe must be self-contained and isolated, $dQ = 0$ for the full universe, and this means that

$$\Delta S \geq 0, \qquad \text{(Thermodynamic Universe)} \tag{1.11.83}$$

Again, equality holds in any *reversible* process. Equation 12.65 is known as the *second law of thermodynamics*. It is a statement, not about the system alone, but about the full thermodynamic universe. The second law states that the only direction for spontaneous changes in the entropy is an increase. Processes for which $\Delta S < 0$ are not possible. Now since $S = k_B \ln \Omega$,

$$\Delta S = k_B \ln \left(\frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}} \right) \geq 0 \tag{1.11.84}$$

We see that an irreversible process must increase the number of microscopic states available to the thermodynamic universe.

The third law of thermodynamics asks what happens to the entropy as $T \to 0$, and this can be easily seen from the Boltzmann relation $S = k_B \ln \Omega$ and our definition of classical microstates. Since

$$\left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} N k_B T \tag{1.11.85}$$

and the energy is equipartitioned among all of the kinetic energy contributions, as $T \to 0$, the only possibility is that all of the momenta (and velocities) of the particles become identically 0. When this happens, the particles stop moving, and their positions become "frozen" into one particular choice. Thus, in the sense of a microcanonical ensemble, there can be only one microstate available to the system, and this will be the global minimum of the potential energy $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Thus, we see that $\Omega \to 1$, and, therefore, $S \to 0$, which is known as the *third law of thermodynamics*.

The third law of thermodynamics makes it possible to calculate entropy changes thermodynamics, as it provides us with a reference states at which we always know the absolute entropy, namely, at $T = 0$. Recall from the first law of thermodynamics that if the

number of moles of a system remains fixed, then

$$\Delta E = Q_{\text{rev}} + W_{\text{rev}} = Q_{\text{rev}} - P\,dV \tag{1.11.86}$$

Thus,

$$Q_{\text{rev}} = \Delta(E + PV) = \Delta H \tag{1.11.87}$$

where H is the enthalpy. Thus, for an infinitesimal change, $dQ_{\text{rev}} = dH$. However, the definition of the constant- pressure heat capacity is

$$C_P(T) = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.11.88}$$

This implies that we can compute entropy changes from the heat capacity as

$$\Delta S = \int_0^T \frac{dQ_{\text{rev}}}{T} = \int_0^T \frac{C_P(T')}{T'} dT' \tag{1.11.89}$$

This relation will become important as we begin to study phase transitions.

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1.12: Introduction to the Thermodynamics of Phase Transitions

Phase Diagrams

The different phases of substances are characterized by different ranges of thermodynamic variables in which these phases are the stable phases. These ranges can be represented on a diagram in which two or more of the thermodynamic state variables are plotted against each other and these different regions are indicated, together with boundary lines separating them. Such a diagram is called a *phase diagram*.

An example of a phase diagram for a normal substance, here benzene, is shown in the figure below. The diagram shows definite ranges of pressure P and temperature T for which the solid, liquid, and gas phases are stable. The line separating the solid and liquid phases is called the *melting curve*, that separating the liquid and gas phases is called the *boiling curve*, and that separating the gas and solid phases is called the *sublimation curve*. Along these lines, the two phases on either side coexist. Hence, these lines are also often referred to as *coexistence curves*. These three lines meet in a point called the *triple point*, at which all three phases coexist. In the right panel, we can expand the temperature axis by plotting $\ln P$ against T, and when we do this, we see that the liquid-gas coexistence curve ends in a point, known as the *critical point*. In the region of the phase diagram to the right of this point, the system exists in a phase known as a *supercritical fluid*. In our study of the van der Waals equation, we showed that the critical point is the point at which we just begin to see the onset of cooperative effects that lead to a phase transition from gas to liquid.

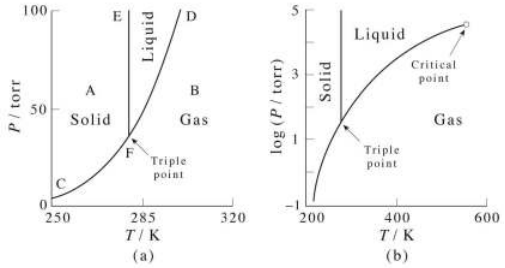


Figure 13.1: Phase diagram of benzene showing P vs. T (left) and $\ln P$ vs. T (right).

A simple phase diagram such as that shown in Figure 13.1 belies a rich complexity of behavior, particularly, in the solid region of the phase diagram, where a variety of solid structures can exist. These are the polymorphs first discussed in lecture 12 on free energies. Each of these solid phases will correspond to a different region in the phase diagram in which it is the most stable of the different solid phases. These different phases will appear in the phase diagram when the pressure axis is expanded. The figure below, for example, shows the solid part of the phase diagram for benzene, showing a wide variety of polymorphs. Each of these different solid phases has its own unique crystal structure, unit cell, and space group.

In normal systems, the slope of the solid-liquid coexistence curve is slightly positive for the reason that the solid phase has a greater density than the liquid phase near the coexistence temperature. If this is the case, then at higher pressures, it takes a higher temperature to get the system to undergo a transition from solid to liquid, since the solid phase will be preferred under conditions of extreme compression.

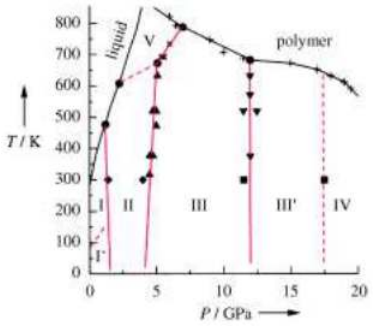


Figure 13.2: Solid phase diagram of benzene.

However, there are a few liquids whose solid phase is less dense than the liquid phase in the coexistence region. One of these is water, which is the reason that ice floats in water. In fact, water has its maximum density at around $4°C$ rather than at $0°C$, its freezing point at standard pressure. The water phase diagram is shown in the figure below: Here we see the slight slope to the left of the solid-liquid coexistence line. As with benzene, the solid region of the phase diagram of water also exhibits a rich variety of different structures, the ice polymorphs, not shown in the phase diagram above. Again, however, if the pressure axis is expanded, these show up. The figure below shows just a few of the known ice polymorphs (more were discussed in class):

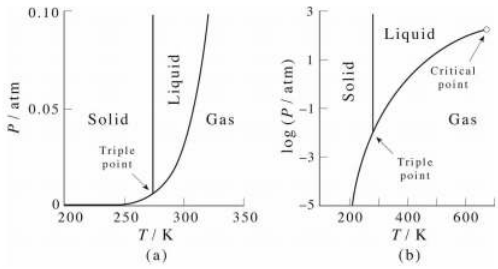


Figure 13.3: Phase diagram of water.

Gibbs Free Energy and Phase Transitions

The Gibbs free energy is a particularly important function in the study of phases and phase transitions. The behavior of $G(N,P,T)$, particularly as a function of P and T, can signify a phase transition and can tell us some of the thermodynamic properties of different phases.

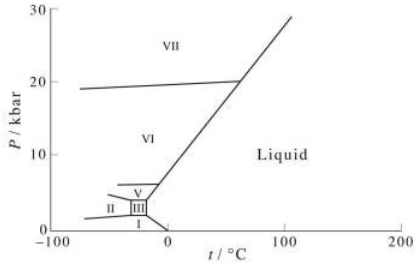


Figure 13.4: Some of the ice polymorphs.

Consider, first, the behavior of G vs. T between the solid and liquid phases of benzene: We immediately notice several things. First, although the free energy is continuous across the phase transition, its first derivative, $\partial G/\partial T$ is not: The slope of $G(T)$ in the solid region is different from the slope in the liquid region. When the first derivative of the free energy with respect to one of its dependent thermodynamic variables is discontinuous across a phase transition, this is an example of what is called a *first order phase transition*. The solid-liquid-gas phase transition of most substances is first order. When the free energy exhibits continuous first derivatives but discontinuous second derivatives, the phase transition is called *second order*. Examples of this type of phase transition are the order-disorder transition in paramagnetic materials.

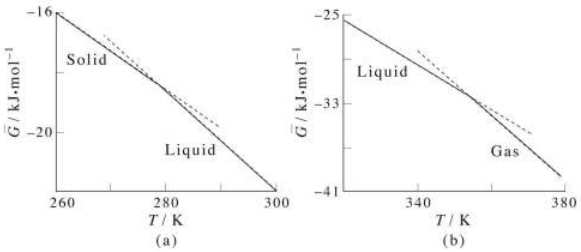


Figure 13.5: Behavior of the Gibbs free energy across the solid-liquid phase (left) and liquid-gas (right) transitions for benzene.

Now, recall that

$$S = -\frac{\partial G}{\partial T} \tag{1.12.1}$$

Consider the slopes in the solid and liquid parts of the graph:

$$\frac{\partial G^{(\text{solid})}}{\partial T} = -S^{(\text{solid})}, \qquad \frac{\partial G^{(\text{liquid})}}{\partial T} = -S^{(\text{liquid})} \tag{1.12.2}$$

However, since

$$\frac{\partial G^{(\text{liquid})}}{\partial T} < \frac{\partial G^{(\text{solid})}}{\partial T} \tag{1.12.3}$$

(*note that the slopes are all negative, and the slope of the liquid line is more negative than that of the solid line*), it follows that $-S^{(\text{liquid})} < -S^{(\text{solid})}$ or $S^{(\text{liquid})} > S^{(\text{solid})}$. This is what we might expect considering that the liquid phase is higher in entropy than the solid phase. The same argument can be made with regards to the gaseous phase.

Similarly, if we consider the dependence of G on pressure, we obtain a curve like that shown in the figure below:

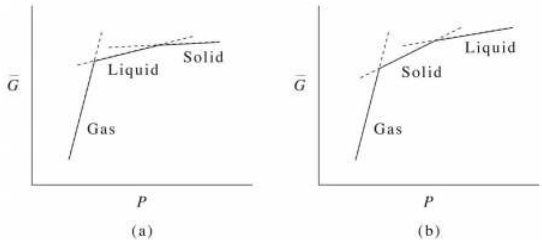


Figure 13.6: Dependence of the Gibbs free energy as a function of pressure for benzene (left) and water (right). For benzene, the temperature is above the triple point, whereas for water, it is set below triple point.

As noted previously, here again, we see that the first derivative of $\bar{G}(P)$ is discontinuous, signifying a first-order phase transition. Recalling that the average molar volume is

$$\bar{V} = \frac{\partial \bar{G}}{\partial P} \tag{1.12.4}$$

From the graph, we see that the slopes obey

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{liquid})} > \bar{V}^{(\text{solid})} \tag{1.12.5}$$

as one might expect for a normal substance like benzene at a temperature above its triple point. Because the temperature is above the triple point, the free energy follows a continuous path (even though it is not everywhere differentiable) from gas to liquid to solid.

On the other hand, for water, we see something a bit different, namely, that

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{solid})} > \bar{V}^{(\text{liquid})} \tag{1.12.6}$$

at a temperature below the triple point. This, again, indicates, the unusual property of water that its solid phase is less dense than its liquid phase in the coexistence region.

Interestingly, if we look at how the plot of $G(P)$ changes with T, we obtain a plot like that shown below: Below the triple point, it is easy to see from the benzene phase diagram that the system proceeds directly from solid to gas. There is a liquid curve on this plot that is completely disconnected from the gas-solid curve, suggesting that, below the triple point, the liquid state can exist metastably if at all. AT the triple point, the solid can transition into the liquid or gas phases depending on the value of the free energy. Near the critical temperature, we see the liquid-gas transition line, while the solid line is disconnected. Above the critical temperature, the system exists as a supercritical fluid, which is shown on the lower line, and this line now shows derivative discontinuity.

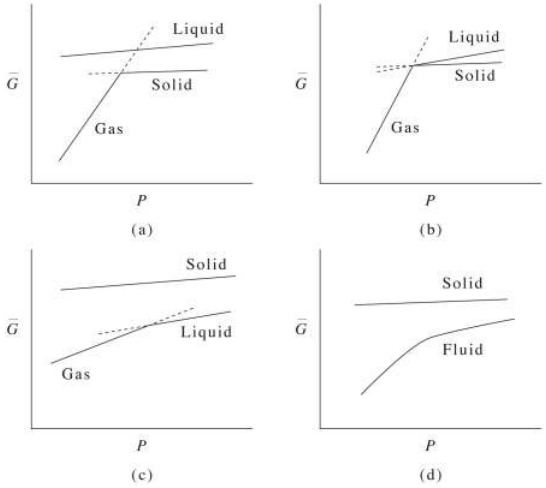


Figure 13.7: Behavior of the Gibbs free energy as a function of P across different phases at different temperatures for benzene. (a): Temperature is less than the triple point; (b): Temperature is equal to the triple point; (c): Temperature is just below the critical temperature; (d): Temperature is greater than the critical temperature.

n-Dependence of the Gibbs Free Energy

Recall that we can express $G(N,P,T)$ equivalently as $G(n,P,T)$, where n is the number of moles. According to Euler's theorem,

$$G(n,P,T) = n\frac{\partial G}{\partial n} = n\mu(P,T) \tag{1.12.7}$$

Therefore,

$$\frac{\partial G}{\partial n} = \mu(P,T) \tag{1.12.8}$$

Now consider the liquid phase of a substance in equilibrium with its vapor. Let there be n_l moles of liquid, and n_g moles of gas. If n is the total number of moles of the substance in the system, then $n_l + n_g = n$. Suppose now that dn_l moles of liquid are transferred to the gas phase. Since $dn = 0$, it follows that

$$\begin{aligned} dn_l + dn_g &= 0 \\ dn_l &= -dn_g \end{aligned} \tag{1.12.9}$$

The Gibbs free energy G depends on both n_l and n_g, i.e., $G = G(n_l, n_g, P, T)$. In addition, the total Gibbs free energy $G(n_l, n_g, P, T)$ is a sum of Gibbs free energies for the liquid and gas phases:

$$G(n_l, n_g, P, T) = G_l(n_l, P, T) + G_g(n_g, P, T) \tag{1.12.10}$$

The change dG in the Gibbs free energy in this transfer is, therefore,

$$dG = \left(\frac{\partial G}{\partial n_l}\right)_{P,T} dn_l + \left(\frac{\partial G}{\partial n_g}\right)_{P,T} dn_g \tag{1.12.11}$$

$$= \left(\frac{\partial G_l}{\partial n_l}\right)_{P,T} dn_l + \left(\frac{\partial G_g}{\partial n_g}\right)_{P,T} dn_g \tag{1.12.12}$$

$$= \mu_l(P,T)dn_l + \mu_g(P,T)dn_g \tag{1.12.13}$$

$$= [\mu_l(P,T) - \mu_g(P,T)]\, dn_l \tag{1.12.14}$$

In equilibrium, $dG = 0$, so from the above, it follows that

$$\begin{aligned} [\mu_l(P,T) - \mu_g(P,T)]\, dn_l &= 0 \\ \mu_l(P,T) &= \mu_g(P,T) \end{aligned} \tag{1.12.15}$$

Hence, in equilibrium, the chemical potentials in the liquid and gas phases are equal. Recall, however, that the chemical potential is the work needed to increase the number of moles of a substance by 1 moles. Therefore, in equilibrium the work needed to increase the number of moles of the gas and liquid phases is the same.

Away from equilibrium, the sign of dG tells us the direction of the matter transfer. Thus, if $dG < 0$, then matter transfer is spontaneous. Here, we need to consider two cases. First, suppose $\mu_g > \mu_l$. Then, for dG to be negative, $dn_l > 0$, which means that the liquid will increase by dn_l until $dG = 0$. This is what we would expect given that the work needed to add matter to the liquid phase is less than that of the gas phase. On the other hand, suppose $\mu_g < \mu_l$. Then, we need $dn_l < 0$, and the liquid phase will decrease by dn_l moles until $dG = 0$. Again, less work is needed to add matter to the gas phase in this case, hence, the direction of matter transfer is as expected.

Enthalpies and Phase Changes

Recall that the Gibbs free energy has two contributions since $G = H - TS$. The behavior of the enthalpy H is also interesting when phase changes occur because of the discontinuous change in the isobaric heat capacity $C_P(T)$ across a phase boundary.

The constant-pressure heat capacity C_P is given by

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.12.16}$$

For an ideal gas, C_P is independent of temperature, however, for non-ideal systems, C_P does depend on T :

$$C_P(T) = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.12.17}$$

If we wish to consider the reaction enthalpy at a temperature other than that of the standard state, where enthalpies are tabulated, we can use Equation 1.12.17 to obtain the enthalpy at the desired temperature. Integrating both sides of Equation 1.12.17 from a temperature T_1 to T_2, we obtain

$$\int_{T_1}^{T_2} C_P(T)\, dT = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_P dT \tag{1.12.18}$$

$$\int_{T_1}^{T_2} C_P(T)\, dT = H(T_2) - H(T_1) \tag{1.12.19}$$

The use of Equation 1.12.19, of course, assumes that the $H(T)$ is everywhere smooth and differentiable, so that it can be integrated.

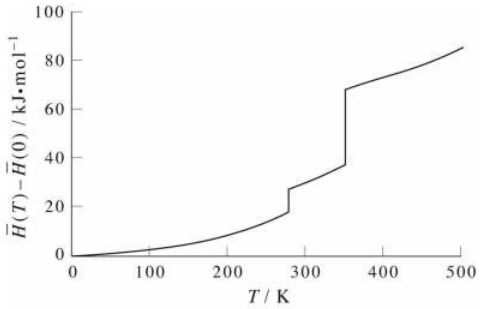


Figure 13.8: Plot of molar enthalpy $\bar{H}(T) - \bar{H}(0)$ for benzene. Discontinuities in the plot occur at points of phase transitions from solid to liquid T_{melt} and from liquid to gas T_{vap}.

However, if we plot the molar enthalpy difference $\bar{H}(T) - \bar{H}(0)$ for a real substance such as benzene, we find a curve like that shown in figure above. There are two temperatures at which $H(T)$ exhibits a discontinuity. These two temperatures are the melting temperature T_{melt} of the solid and the vaporization temperature T_{vap} of the liquid. According to our discussion of phase changes, the heat needed to effect these two phase changes are $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$, respectively. At these temperatures, $C_P = \partial H/\partial T$ diverges, and we cannot smoothly integrate through these divergences. In fact, divergence of the heat capacity is one of the signatures of a phase transition. As long as $T < T_{\text{melt}}$, we can smoothly integrate $C_P(T)$ to obtain a value for $H(T)$:

$$H(T) - H(0) = \int_0^T C_P(T')\, dT' \tag{1.12.20}$$

However, if we are interested in a temperature $T > T_{\text{melt}}$, then we must treat the discontinuity as a special point. Fortunately, we already know the enthalpy change at this point, i.e., $\Delta_{\text{fus}}H$, and we can simply add it in. Thus, for $T > T_{\text{melt}}$, we would calculate

$H(T)$ as follows:

$$H(T) - H(0) = \int_0^{T_{\text{melt}}} C_P(T')\,dT' + \Delta_{\text{fus}}H + \int_{T_{\text{melt}}}^{T} C_P(T')\,dT' \tag{1.12.21}$$

The same holds for $T > T_{\text{vap}}$. When we reach the discontinuity at T_{vap}, we simply add in the enthalpy of vaporization $\Delta_{\text{vap}}H$:

$$\begin{aligned} &H(T) - H(0) \\ &= \int_0^{T_{\text{melt}}} C_P(T')\,dT' + \Delta_{\text{fus}}H + \int_{T_{\text{melt}}}^{T_{\text{vap}}} C_P(T')\,dT' + \Delta_{\text{vap}}H + \int_{T_{\text{vap}}}^{T} C_P(T')\,dT' \end{aligned} \tag{1.12.22}$$

Example 13.1

Consider the reaction

$$CO(g) + H_2O(g) \longrightarrow H_2(g) + CO_2(g)/n$$

For this reaction, the heat capacity has the following temperature dependence

$$C_P(T) = a + bT + cT^2/n$$

where a, b, and c are constants. Calculate the reaction enthalpy at $800\ \text{K}$ for this reaction given the following data: For CO: $a = 26.86$, $b = 6.99 \times 10^{-3}$, $c = 8.20 \times 10^{-7}$, for H_2O: $a = 30.98$, $b = 9.62 \times 10^{-3}$, $c = 11.84 \times 10^{-7}$, for CO_2: $a = 25.98$, $b = 43.51 \times 10^{-3}$, $c = -184.32 \times 10^{-7}$, for H_2: $a = 26.08$, $b = -0.84 \times 10^{-3}$, $c = 20.13 \times 10^{-7}$. The units of a, b, and c are $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$, and $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-3}$, respectively. Standard-state formation enthalpies for CO, H_2O, CO_2, and H_2 are $-110.52\ \text{kJ/mol}$, $-241.82\ \text{kJ/mol}$, $-393.51\ \text{kJ/mol}$, and $0\ \text{kJ/mol}$, respectively.

Solution

Since this is already a gas-phase reaction, we do not need to worry about melting or vaporization, so we can smoothly integrate $C_P(T)$ from the standard state, where $T = 298\ \text{K}$ to the desired $800\ \text{K}$. Let us first obtain the formation enthalpies at $800\ \text{K}$. Since our reference state is $298\ \text{K}$, the integral we need is

$$\Delta_f H^{(800)} = \Delta_f H^\circ + \int_{T_0}^{T_f} C_P(T)\,dT \tag{1.12.23}$$

where $T_0 = 298\ \text{K}$ and $T_f = 800\ \text{K}$. The integral is

$$\int_{T_0}^{T_f} C_P(T)\,dT = a(T_f - T_0) + \frac{1}{2}b(T_f^2 - T_0^2) + \frac{1}{3}c(T_f^3 - T_0^3) \tag{1.12.24}$$

Plugging in the data, we obtain

$$\begin{aligned} \Delta_f H^{(800)}(CO) &= -94.981\ \text{kJ/mol} \\ \Delta_f H^{(800)}(CO_2) &= -370.883\ \text{kJ/mol} \\ \Delta_f H^{(800)}(H_2O) &= -223.731\ \text{kJ/mol} \\ \Delta_f H^{(800)}(H_2) &= 14.668\ \text{kJ/mol} \end{aligned} \tag{1.12.25}$$

Therefore, the overall reaction enthalpy is

$$\begin{aligned} \Delta_f H^{(800)} &= \Delta_f H^{(800)}(H_2) + \Delta_f H^{(800)}(CO_2) - \Delta_f H^{(800)}(H_2O) - \Delta_f H^{(800)}(CO) \\ &= 14.668 - 370.883 + 94.981 + 223.731 = -37.503\ \text{kJ/mol} \end{aligned} \tag{1.12.26}$$

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1.13: The Clapeyron equation, Gibbs phase rule, and Classical Nucleation Theory

The Clapeyron Equation

The Clapeyron attempts to answer the question of what the shape of a two-phase coexistence line is. In the $P-T$ plane, we see the a function $P(T)$, which gives us the dependence of P on T along a coexistence curve.

Consider two phases, denoted α and β, in equilibrium with each other. These could be solid and liquid, liquid and gas, solid and gas, two solid phases, et. Let $\mu_\alpha(P,T)$ and $\mu_\beta(P,T)$ be the chemical potentials of the two phases. We have just seen that

$$\mu_\alpha(P,T) = \mu_\beta(P,T) \tag{1.13.1}$$

Next, suppose that the pressure and temperature are changed by dP and dT. The changes in the chemical potentials of each phase are

$$d\mu_\alpha(P,T) = d\mu_\beta(P,T) \tag{1.13.2}$$

$$\left(\frac{\partial \mu_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \mu_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \mu_\beta}{\partial T}\right)_P dT \tag{1.13.3}$$

However, since $G(n,P,T) = n\mu(P,T)$, the *molar* free energy $\bar{G}(P,T)$, which is $G(n,P,T)/n$, is also just equal to the chemical potential

$$\bar{G}(P,T) = \frac{G(n,P,T)}{n} = \mu(P,T) \tag{1.13.4}$$

Moreover, the derivatives of $\bar{G}$ are

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}, \qquad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \tag{1.13.5}$$

Applying these results to the chemical potential condition in Equation 1.13.3, we obtain

\[\begin{align} \left(\dfrac{\partial \bar{G}_\alpha}{\partial P} \right)_T dP + \left(\dfrac{\partial \bar{G}_\alpha}{\partial T} \right)_P dT &= \left(\dfrac{\partial \bar{G}_\beta}{\partial P} \right)_T dP + \left(\dfrac{\partial \bar{G}_\beta}{\partial T} \right)_P dT \\

Misplaced &

Dividing through by dT, we obtain

\[\begin{align} \bar{V}_\alpha \dfrac{\partial P}{\partial T} - \bar{S}_\alpha &= \bar{V}_\beta \dfrac{\partial P}{\partial T} - \bar{S}_\beta \\

\[5pt] (\bar{V}_\alpha - \bar{V}_\beta) \dfrac{\partial P}{\partial T} &= \bar{S}_\alpha - \bar{S}_\beta \\

Misplaced &

The importance of the quantity dP/dT is that is represents the slope of the coexistence curve on the phase diagram between the two phases. Now, in equilibrium $dG = 0$, and since $G = H - TS$, it follows that $dH = T\,dS$ at fixed T. In the narrow temperature range in which the two phases are in equilibrium, we can assume that H is independent of T, hence, we can write $S = H/T$. Consequently, we can write the molar entropy difference as

$$\bar{S}_\alpha - \bar{S}_\beta = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T} \tag{1.13.6}$$

and the pressure derivative dP/dT becomes

$$\frac{dP}{dT} = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T(\bar{V}_\alpha - \bar{V}_\beta)} = \frac{\Delta_{\alpha\beta}\bar{H}}{T\Delta_{\alpha\beta}\bar{V}} \tag{1.13.7}$$

a result known as the **Clapeyron equation**, which tells us that the slope of the coexistence curve is related to the ratio of the molar enthalpy between the phases to the change in the molar volume between the phases. If the phase equilibrium is between the solid and liquid phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{fus}}$ and $\Delta\bar{V}_{\text{fus}}$, respectively. If the phase equilibrium is between the liquid and gas phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{vap}}$ and $\Delta\bar{V}_{\text{vap}}$, respectively.

For the liquid-gas equilibrium, some interesting approximations can be made in the use of the Clapeyron equation. For this equilibrium, Equation 1.13.7 becomes

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T(\bar{V}_g - \bar{V}_l)} \tag{1.13.8}$$

In this case, $\bar{V}_g \gg \bar{V}_l$, and we can approximate Equation 1.13.8 as

$$\frac{dP}{dT} \approx \frac{\Delta\bar{H}_{\text{vap}}}{T\bar{V}_g} \tag{1.13.9}$$

Suppose that we can treat the vapor phase as an ideal gas. Certainly, this is not a good approximation so close to the vaporization point, but it leads to an example we can integrate. Since $PV_g = nRT$, $P\bar{V}_g = RT$, Equation 1.13.9 becomes

\[\begin{align} \dfrac{dP}{dT} &= \dfrac{\Delta \bar{H}_\text{vap} P}{RT^2} \\

\[5pt] \dfrac{1}{P} \dfrac{dP}{dT} &= \dfrac{\Delta \bar{H}_\text{vap}}{RT^2} \\

Misplaced &

which is called the ***Clausius-Clapeyron equation***. We now integrate both sides, which yields

$$\ln P = -\frac{\Delta\bar{H}_{\text{vap}}}{RT} + C \tag{1.13.10}$$

where C is a constant of integration. Exponentiating both sides, we find

$$P(T) = C' e^{-\Delta\bar{H}_{\text{vap}}/RT} \tag{1.13.11}$$

which actually has the wrong curvature for large T, but since the liquid-vapor coexistence line terminates in a critical point, as long as T is not too large, the approximation leading to the above expression is not that bad.

If we, instead, integrate both sides, the left from P_1 to P_2, and the right from T_1 to T_2, we find

\[\begin{align} \int_{P_1}^{P_2} d \: \text{ln} \: P &= \int_{T_1}^{T_2} \dfrac{\Delta \bar{H}_\text{vap}}{RT^2} dT \\

\[5pt] \text{ln} \: \left(\dfrac{P_2}{P_1} \right) &= -\dfrac{\Delta \bar{H}_\text{vap}}{R} \left(\dfrac{1}{T_2} - \dfrac{1}{T_1} \right) \\

Misplaced &

assuming that $\Delta\bar{H}_{\text{vap}}$ is independent of T. Here P_1 is the pressure of the liquid phase, and P_2 is the pressure of the vapor phase. Suppose we know P_2 at a temperature T_2, and we want to know P_3 at another temperature T_3. The above result can be written as

$$\ln\left(\frac{P_3}{P_1}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{1.13.12}$$

Subtracting the two results, we obtain

$$\ln\left(\frac{P_2}{P_3}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_3}\right) \tag{1.13.13}$$

so that we can determine the vapor pressure at any temperature if it is known as one temperature.

In order to illustrate the use of this result, consider the following example:

Example 1.13.1

At 1 bar, the boiling point of water is 373 K. At what pressure does water boil at 473 K? Take the heat of vaporization of water to be 40.65 kJ/mol.

Solution

Let $P_1 = 1$ bar and $T_1 = 373$ K. Take $T_2 = 473$ K, and we need to calculate P_2. Substituting in the numbers, we find

\[\begin{align} \text{ln} \: P_2(\text{bar}) &= -\dfrac{(40.65 \: \text{kJ/mol})(1000 \: \text{J/kJ})}{8.3145 \: \text{J/mol} \cdot \text{K}} \left(\dfrac{1}{473 \: \text{K}} - \dfrac{1}{373 \: \text{K}} \right) = 2.77 \

Misplaced &

Gibbs Phase Rule

In any one-component system with three phases, there is only one point at which all three phases coexist in equilibrium. This is known as the *triple point*. Although the Gibbs free energy G is a function of n, P, and T, $G = G(n, P, T)$, if we allow ourselves to treat P and T as experimental control parameters, as is done when we construct a phase diagram, then n is determined by the equation of state. P and T are both intensive properties.

Now suppose we have a multicomponent system. When we have more than one component, we have additional intensive properties that could potentially be additional degrees of freedom that determine the dimensionality of the phase diagram. If the phase diagram has a dimensionality higher than that of a plane (two dimensions), then triple points could become lines, planes, curved surfaces, or hypersurfaces. Thus, it is important to have a way of determining how many actual experimental control variables we have in a multicomponent system. This number is determined by the number of thermodynamic conditions that exist among the intensive properties. We will now derive a relation that accounts for these conditions and yields the total number of degrees of freedom or experimental control parameters – this relation is known as the *Gibbs phase rule*.

Suppose a system has k components and can exist in p phases. An example would be a three-component system consisting of H_2O, CH_3OH, and CH_3CH_2OH. The Gibbs free energy G is now a function of $n_1, \ldots, n_k$, P, and T: $G = G(n_1, \ldots, n_k, P, T)$. The total number of moles n is still determined by the equation of state if we allow P and T to be experimental control parameters. However, we now have a condition

$$n_1 + n_2 + \cdots + n_k = n \tag{1.13.14}$$

We can now introduce additional intensive parameters by dividing both sides by n, which yields

$$\frac{n_1}{n} + \frac{n_2}{n} + \cdots + \frac{n_k}{n} = 1 \tag{1.13.15}$$

We defined

$$X^{(i)} = \frac{n_1}{n} \tag{1.13.16}$$

called the *mole fraction* of component i. Clearly, we must have

$$X^{(1)} + X^{(2)} + \cdots + X^{(k)} = 1 \tag{1.13.17}$$

Moreover, $X^{(i)}$ is an intensive property.

Suppose, for starters, that $k = 1$, but we have p phases. If α and β denote a pair of phases, then at a p-phase coexistence point, we have a set of conditions from the chemical potential equalization that take the form

$$\mu_\alpha(P, T) = \mu_\beta(P, T) \tag{1.13.18}$$

For example, if we had three phases, solid, liquid, and gas, the conditions would be

$$\mu_{\text{liq}}(P, T) = \mu_{\text{gas}}(P, T), \qquad \mu_{\text{liq}}(P, T) = \mu_{\text{solid}}(P, T), \qquad \mu_{\text{solid}}(P, T) = \mu_{\text{gas}}(P, T) \tag{1.13.19}$$

However, by the transitive property, the third condition follows from the first two, so it's not an independent condition. In fact, we have only two independent conditions. In general, if we have p phases, we have $p - 1$ such conditions.

Now if we have k components, then we have $p-1$ such conditions for each phase, giving a total of $k(p-1)$ total conditions from chemical potential equalization. The fact that the mole fractions in each phase must sum to 1 gives us additional condition. Let $X_\alpha^{(i)}$ be the mole fraction of component i in phase α. For each phase, we have a condition

$$X_\alpha^{(1)} + X_\alpha^{(2)} + \cdots + X_\alpha^{(k)} = 1 \tag{1.13.20}$$

This gives us p additional conditions. Hence, the total number of conditions we have is $k(p-1)+p$. Although the equation of state constitutes, in principle, another condition, we have already taken it into account by positing that the total number of moles n is determined if we know P and T.

Now the total number of mole fractions is k for each phase for a total of kp mole fractions. In addition, if we add P and T as additional parameters, then the total number of intensive thermodynamic parameters we can tune is $kp+2$. If we subtract from this the number of conditions (also the number of constraints), we obtain the number of degrees of freedom d as

\[\begin{array}{rcl} d & = & kp + 2 - k(p - 1) - p \\

\[5pt] & = & kp + 2 - kp + k - p \\

Misplaced &

The condition

$$d = k - p + 2 \tag{1.13.21}$$

is known as the *Gibbs phase rule*.

As an example, suppose we have $k=3$ components and $p=3$ phases. Then the number of degrees of freedom is

$$d = 3 - 3 + 2 = 2 \tag{1.13.22}$$

which we could take to be P and T. However, we could also take these to be P and one of the mole fractions or T and one of the mole fractions.

As another example, consider water, which has three phases, ice, water, steam. Here, we have $k=1$ and $p=3$. Thus,

$$d = 1 - 3 + 2 = 0 \tag{1.13.23}$$

which means that when all three phases are in coexistence, the number of degrees of freedom is 0. Hence, there can be only one point, i.e. one value of P and one value of T, at which this coexistence occurs, which we call the triple point. However, this explains why the triple point is a point and not a structure of higher dimension.

Classical Nucleation Theory

Having looked at phase diagrams in some detail, we now turn our attention to the process by which phase transitions occur. In particular, we will consider a phenomenological theory known as *classical nucleation theory*. Let us consider it in the special case of the solid-liquid transition, i.e., the melting transition. In this case, if we are in the solid phase and far from the melting point, then we have the condition $\mu_s < \mu_l$, which tells us that the solid phase is more stable (remember that chemical potentials are also molar free energies, and the solid phase should have a lower free energy far from the melting point).

As we approach the melting point, the liquid phase becomes the more stable of the two phases, and we have $\mu_s > \mu_l$ or $\mu_l - \mu_s < 0$. The solid phase now becomes a *metastable* phase. This means that, even though the liquid phase is the more stable of the two phases, there is a significant free energy barrier that must be crossed in order for the system to undergo a transition from solid to liquid. How do we characterize this barrier? In order to do this, we introduce a microscopic coordinate in the system that is capable of following the progress of the melting process. Such a coordinate is called a *reaction coordinate*. In general, a reaction coordinate is some function of the atomic positions that is capable of following a particular process, such as chemical reaction, a diffusion process, or a phase transition.

Classical nucleation theory (CNT) posits that as a solid is heated close to its melting point, a liquid *nucleus* can form in the solid, and as this nucleus grows, eventually, the system will melt completely, transforming from solid to liquid. If we assume that this

nucleus is a sphere of radius r, then r can be viewed as the reaction coordinate. As r increases, the size of the liquid nucleus increases, and ultimately, the system melts. This process is illustrated in Figure 14.1 below.

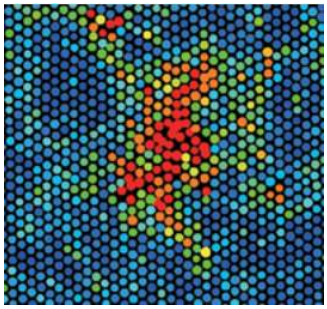


Figure 14.1: Illustration of a liquid nucleus.

The free energy to form a nucleus of radius r will be a function of r, which we denote as $\Delta G(r)$. Such a coordinate-dependent free energy is called a *free energy profile*. The free energy needed to form such a nucleus has two contributions. First, work is needed to form the surface of the nucleus, which is an interface between the solid and the liquid. As these two things do not naturally fit together, it is not energetically favorable to form the surface of the nucleus. Let γ_s denote the surface tension of the nucleus, which has units of energy per unit area. The area of the nucleus is $4\pi r^2$, so this contribution to the free energy is $4\pi r^2 \gamma_s$. On the other hand, since $\mu_l < \mu_s$, forming a liquid nucleus of volume $4\pi r^3/3$ is favorable. If $\Delta\mu$ represents the chemical potential difference per unit volume, then given that $\Delta\mu < 0$, this contribution to the free energy $(4\pi r^3/3)\Delta\mu$ is negative. Hence, we have a balance between the volume and surface area terms, and the total free energy in the CNT is

$$\Delta G(r) = \frac{4}{3}\pi r^3 \Delta\mu + 4\pi r^2 \gamma_s \tag{1.13.24}$$

If we plot this free energy as a function of r, we obtain a curve of the form show in Figure 14.2. We see from the free energy profile that there is a significant barrier at a particular radius r_{max}. The height of the barrier is $\Delta G(r_{max})$. To find what this radius is, we need to maximize ΔG. We take the derivative of $\Delta G(r)$ with respect to r and set it equal to 0

\[\begin{align} \dfrac{d \Delta G}{dr} = 4 \pi r^2 \Delta \mu + 8 \pi r \gamma_s &= 0 \\

\[5pt] r \Delta \mu + 2 \gamma_s &= 0 \\

Misplaced &

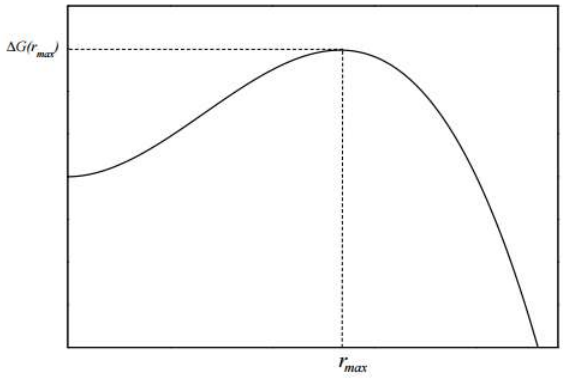


Figure 14.2: Plot of $\Delta G(r)$.

If we evaluate the free energy at this radius, we find the barrier height to be

\[\begin{align} \Delta G(r_\text{max}) &= \dfrac{4}{3} \pi \left(- \dfrac{2 \gamma_s}{\Delta \mu} \right)^3 + 4 \pi \left(- \dfrac{2 \gamma_s}{\Delta \mu} \right)^2 \gamma_s \\

\[5pt] &= -\dfrac{4}{3} \pi \left(\dfrac{8 \gamma_s^3}{(\Delta \mu)^3} \right) \Delta \mu + 4 \pi \left(\dfrac{4 \gamma_s^2}{(\Delta \mu)^2} \right) \gamma_s \\

Misplaced &

For water, for example, the height of the barrier, computed from this formula, would be around $100k_BT$, which corresponds to a barrier of around $50\ \mathrm{kcal/mol}$. Thus, we see that, although the liquid phase is more stable, a very high energy barrier needs to be surmounted, which is a rare event.

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1.14: Introduction to Solutions

Defining Solutions

When two or more substances are combined to form a homogeneous mixture, the result is a multi-component solution. Solutions can be mixtures of multiple liquids, solids and liquids, or solids and solids. If there is a major component, it is called the *solvent*, and the minor components are called the *solutes*. If all components are present in equal amounts, no such distinction is possible.

Characterizing the Microscopic Structure of Solutions Using Statistical Mechanics

When a solid is dissolved in a solvent, it might dissociate or remain intact. If the former, it becomes *solvated*. This means that solvent molecules will form a solvent shell or *solvation shell* around the solute species. The number of such nearest neighbor solvent molecules is called the *coordination number*. Some examples, shown as snapshots from computer simulations of solvation, illustrate the concept of coordination shells and their structures.

Simulations of the aqueous solvation of the Be^{2+} ion show a solvation shell that fluctuates between 6 and 4 water molecules, as the two snapshots below illustrate:

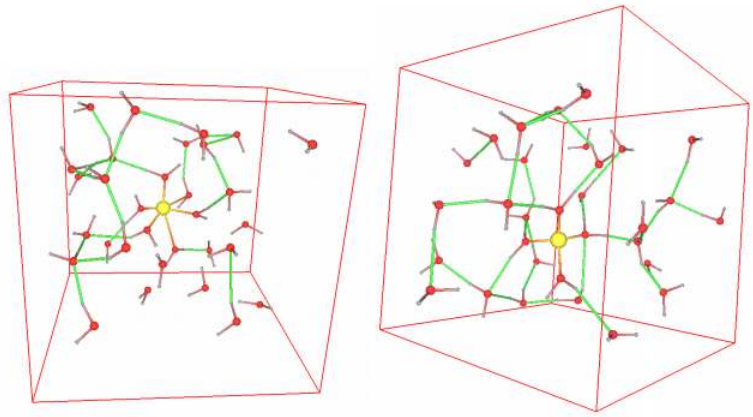


Figure 15.1: Snapshots from a simulation of the Be^{2+} ion in water.

The average is strongly weighted toward a coordination number of four, which is the favored state for this ion.

Several other examples arise in the chemistry of acids and bases. First, consider the case of a strong acid such as HCl, which dissociates into H^+ and Cl^-. What does the solvation of the excess proton look like? First, it is well known that excess protons in water attach to water molecules to form the hydronium ion H_3O^+, which is a highly mobile ion in water (its diffusion constant is roughly 5 times that of the self-diffusion of water molecules). The hydronium ion forms a solvation shell in which it donates three hydrogen bonds to neighboring water molecules as shown in the snapshot below:

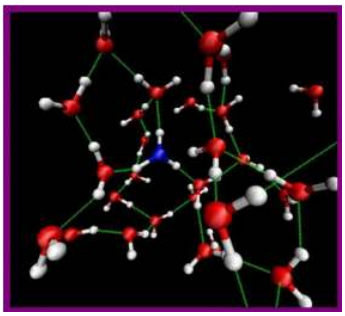


Figure 15.2: Snapshot from a simulation of the hydronium ion in water.

The hydronium ion is transported via conversion between this solvated complex and on in which the excess proton is shared between two water molecules. This process is initiated when a first solvation shell water loses one of its acceptor hydrogen bonds. This is illustrated in the snapshots shown below:

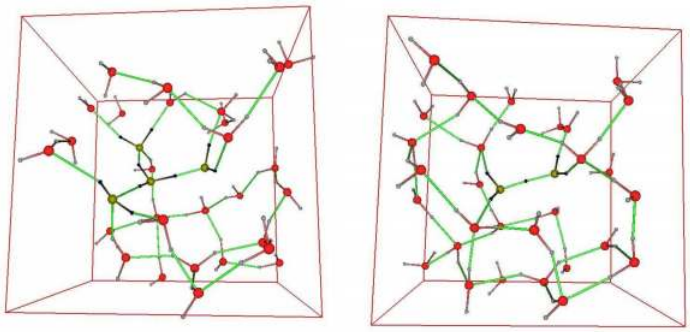


Figure 15.3: Snapshots from a simulation of the transport of H_3O^+ ion in water. The left panel shows shows the hydronium in its normal solvation state. The right panel shows the hydronium diffusing via a structural diffusion process in which one of its protons is transferred to a neighboring water molecule.

Thus, it is clear that hydronium does not diffuse as an intact object but rather as a topological defect in the hydrogen bond network of the water solvent. The structural defect moves from oxygen to oxygen in the network mediated by a series of proton transfer reactions. This type of diffusion is known as *structural diffusion*.

Another example of structural diffusion occurs in basic solutions and describes how the hydroxide ion is transported. Hydroxide is present in aqueous solution when a strong base such as KOH or $NaOH$ is dissolved in water. The snapshot below shows the most probable coordination structure of a hydroxide ion in water:

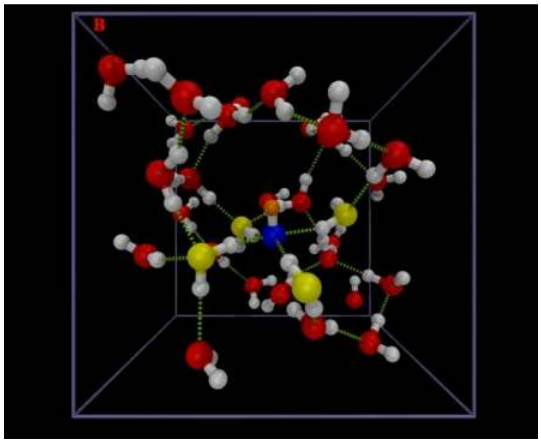


Figure 15.4: Snapshot from a simulation of the hydroxide ion in water.

In this snapshot, we see the hydroxide ion accepting four hydrogen bonds at the oxygen site from neighboring water molecules. At first, this solvation pattern might seem strange if we think of the Lewis structure of the hydroxide ion. The Lewis structure shows three lone pairs of electrons around the hydroxide oxygen. If we regard each lone pair as a hydrogen bond acceptor site, then we might expect hydroxide to accept at most three hydrogen bonds. What allows it to accept four. Here, we can use our understanding of quantum mechanics to help out. The figure below shows a measure of regions of highest probability to find the lone-pair electrons:

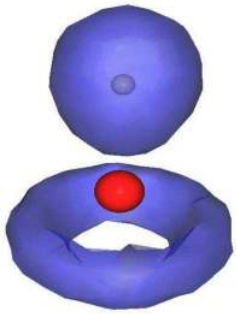


Figure 15.5: Isosurface of high probability regions for finding lone-pair electrons in the hydroxide ion.

From this figure, we see that the lone pairs are completely delocalized into a ring centered on the OH^- bond axis. Given this delocalization of the lone pairs, the number of hydrogen bonds that can be donated to the hydroxide ion depends only on the number of waters that can be packed around the ring. This explains the coordination pattern that is observed in Figure 15.4. The structural diffusion process of the hydroxide ion starts with a change in the number of coordinating water molecules around the oxygen from **4** to **3** as shown in the snapshots below:

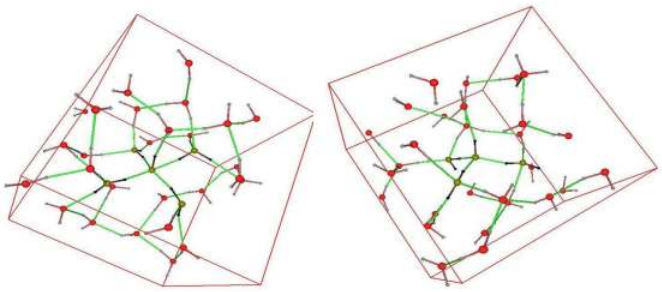


Figure 15.6: Snapshots showing the first step of the structural diffusion process of the hydroxide ion. The process begins with a change in the coordination number of the oxygen from **4** to **3**.

The unusual coordination pattern see for the hydroxide ion is not unique to this ion or to aqueous solutions. Consider the analogous isosurface of Figure 15.5 for the amide ion NH_2^-. This is shown below:

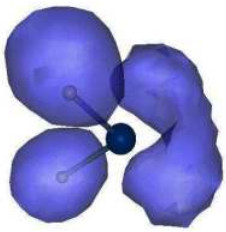


Figure 15.7: Isosurface of high probability regions for finding lone-pair electrons in the amide ion.

If we take NH_2^- in an ammonia solvent, we get solvation patterns such as that shown in the figure below:

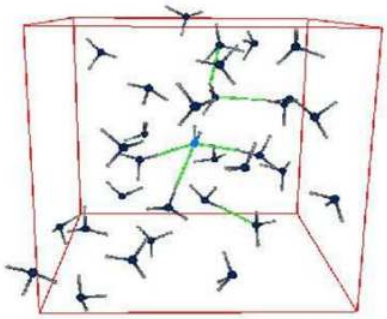


Figure 15.8: Typical solvation pattern of the amide ion in ammonia solvent.

As with the hydroxide ion, we see that the number of coordinating ammonia molecules is determined only by the number that can be packed around the semi-ring seen in Figure 15.7.

Mixtures of liquids are typically characterized on a large length scale, as the snapshots below illustrate:

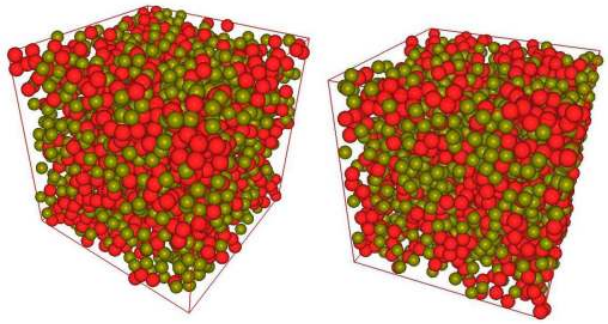


Figure 15.9: Snapshots from a computer simulation of a methanol/water mixture.

These are snapshots from a $50:50$ mixture of methanol and water. The figure shows just the positions of the oxygen atoms in each mixture, red spheres are water oxygens, gold spheres are methanol oxygens. The repulsive nature of the interactions between methanol and water cause the water to form small clusters with the methanols percolating between them.

Characterizing the microscopic nature of solutions amounts to finding the average distances between different components in the solution. When we have solvated ions, for example, we would like to know the average distance between the ion and the coordinating solvent molecules. For liquid-liquid mixtures, we would like to know average distances between molecules either of like type or different types in the solution. Both of these can be addressed using the techniques of neutron or X-ray scattering. How does this allow us to determine average distances? In order to answer this, let us consider a simpler question, that of determining the distance between planes of a simple crystal. The scattering technique used to do this is called *Bragg scattering*, as illustrated in Figure 15.10 below. The wave vectors are related to the wavelength λ of the incident and scattered waves by

$$|\mathbf{k}_i| = |\mathbf{k}_s| = \frac{2\pi}{\lambda} \tag{1.14.1}$$

In Bragg scattering, we look for constructive interference between waves scattered from the top plane and the plane just beneath it. This can only occur if the path difference, which is $2d\sin\psi$ is an integer number of wavelengths, which leads to the Bragg condition

$$2d\sin\psi = n\lambda \tag{1.14.2}$$

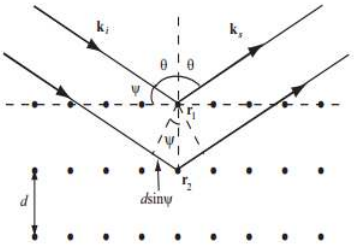


Figure 15.10: Illustration of Bragg scattering from neighboring planes in a crystal.

This allows us to determine the distance d between neighboring crystal planes. Note that the angle θ is related to ψ by

$$\theta = \frac{\pi}{2} - \psi \tag{1.14.3}$$

Thus,

$$\sin\psi = \sin\left(\frac{\pi}{2} - \theta\right) = \cos\theta \tag{1.14.4}$$

Thus, the Bragg condition becomes

$$2d\cos\theta = n\lambda \tag{1.14.5}$$

Now, if we assign position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ as shown in the figure, then we have the following relations between the vector $\mathbf{r}_1 - \mathbf{r}_2$ and the vectors $\mathbf{k}_i$ and $\mathbf{k}_s$:

$$\begin{aligned} -\mathbf{k}_i \cdot (\mathbf{r}_1 - \mathbf{r}_2) &= |\mathbf{k}_i|\,|\mathbf{r}_1 - \mathbf{r}_2|\cos\theta \\ \mathbf{k}_s \cdot (\mathbf{r}_1 - \mathbf{r}_2) &= |\mathbf{k}_s|\,|\mathbf{r}_1 - \mathbf{r}_2|\cos\theta \end{aligned} \tag{1.14.6}$$

If we add these two conditions together, we obtain

$$(\mathbf{k}_s - \mathbf{k}_i) \cdot (\mathbf{r}_1 - \mathbf{r}_2) = (|\mathbf{k}_i| + |\mathbf{k}_s|)\,|\mathbf{r}_1 - \mathbf{r}_2| \cos\theta \tag{1.14.7}$$

$$= \left(\frac{2\pi}{\lambda} + \frac{2\pi}{\lambda}\right) d\cos\theta \tag{1.14.8}$$

$$= \frac{4\pi}{\lambda} d\cos\theta \tag{1.14.9}$$

Define the difference $(\mathbf{k}_s - \mathbf{k}_i)$ as the vector $\mathbf{q}$, known as the *momentum transfer*. For constructive interference, we still have the Bragg condition $2d\cos\theta = n\lambda$. Thus, we can write the Bragg condition as

$$\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2) = 2\pi n \tag{1.14.10}$$

which is equivalent to the condition

$$e^{i\mathbf{q}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} = 1 \tag{1.14.11}$$

The reason for taking the exponential like this is that neutron and X-ray scattering measurements really measure this quantity, since the spatial dependence of a wave form is generally $\exp(i\mathbf{k}\cdot\mathbf{r})$.

Now in a solution, the atoms are constantly in motion due the finite temperature. In addition, all possible pairs are detected in the measurement. This means that we need to sum the exponentials over all particle pairs and take an ensemble average. Alternatively, we can look at the scattering off each individual atom at position $\mathbf{r}_i$, sum over all atoms, and then square to get a *real* scattering intensity. This gives us a function $S(\mathbf{q})$ known as the *scattering function*, which is then given by

$$S(\mathbf{q}) = \frac{1}{N}\left\langle \left| \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i} \right|^2 \right\rangle \tag{1.14.12}$$

For isotropic systems, $S(\mathbf{q})$ should only depend on the magnitude $|\mathbf{q}|$ of $\mathbf{q}$, since there are no preferred directions in space. In this case, it is straightforward to show that $S(q)$ is related to the radial distribution function by

$$S(q) = 4\pi\rho \int_0^\infty dr\, r^2 (g(r) - 1) \frac{\sin qr}{qr} \tag{1.14.13}$$

where the radial distribution function is given by

$$g(r) = \frac{(N-1)}{4\pi\rho r^2 Z(N,V,T)} \int_{|\mathbf{r}_1 - \mathbf{r}_2| = r} e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} d\mathbf{r}_1 \cdots d\mathbf{r}_N \tag{1.14.14}$$

where $\rho = N/V$, and $Z(N,V,T)$ is the configurational partition function. An equivalent way to write $g(r)$ is

$$g(r) = \frac{(N-1)}{4\pi\rho r^2} P(r) \tag{1.14.15}$$

where $P(r)$ is the spatial probability distribution

$$P(r) = \frac{4\pi r^2 V}{Z(N,V,T)} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \tag{1.14.16}$$

If a system contains several chemical species, then radial distribution functions $g_{\alpha\beta}(r)$ among the different species can be introduced. Here, α and β range over the different species, with $g_{\alpha\beta}(r) = g_{\beta\alpha}(r)$. Equation 15.9 then generalizes to

$$S_{\alpha\beta}(q) = 4\pi\rho \int_0^\infty dr\, r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin qr}{qr} \tag{1.14.17}$$

$S_{\alpha\beta}(q)$ are called the *partial structure factors*, and ρ is the full atomic number density.

Thermodynamics of Solutions

A useful quantity to characterize the solution composition is the so-called *mole fraction* defined as follows: Suppose a solution contains $\mathcal{N}$ components. Let there be n_1 moles of component 1, n_2 moles of component 2, ..., $n_\mathcal{N}$ moles of component $\mathcal{N}$. The mole fraction of component j is

$$x_j = \frac{n_j}{\sum_{k=1}^{\mathcal{N}} n_k} \tag{1.14.18}$$

We see, immediately, that $\Sigma_j x_j = 1$. For example, in a two-component solution, there are two mole fractions given by

$$x_1 = \frac{n_1}{n_1 + n_2}, \qquad x_2 = \frac{n_2}{n_1 + n_2} \tag{1.14.19}$$

Concepts such as molarity and molality are generally used to describe the composition of solid-liquid solutions involving dissolved species. Hence, we will hold off on discussing these quantities until we get to this topic.

Next, let us consider the free energy for a two-component solution. There are n_1 moles of component 1 and n_2 moles of component 2. Hence, the Gibbs free energy G is a function $G(n_1, n_2, P, T)$ of the number of moles of each component as well as pressure and temperature. From Euler's Theorem,

$$G(n_1, n_2, P, T) = n_1 \left(\frac{\partial G}{\partial n_1}\right)_{P,T} + n_2 \left(\frac{\partial G}{\partial n_2}\right)_{P,T} = n_1 \mu_1(P, T) + n_2 \mu_2(P, T) \tag{1.14.20}$$

Hence, a change dG in G due to changes in the number of moles of each component as well as pressure and temperature (which changes the chemical potentials) is

$$dG = \mu_1\, dn_1 + \mu_2\, dn_2 + n_1\, d\mu_1 + n_2\, d\mu_2 \tag{1.14.21}$$

At equilibrium, $dG = 0$. If the number of moles of each component remain fixed, then $dn_1 = dn_2 = 0$. Then we are left with

$$n_1\, d\mu_1 + n_2\, d\mu_2 = 0 \tag{1.14.22}$$

This can be expressed as a condition in terms of mole fractions by dividing through by $n_1 + n_2$ to yield

$$\frac{n_1}{n_1 + n_2} d\mu_1 + \frac{n_2}{n_1 + n_2} d\mu_2 = 0 \tag{1.14.23}$$

$$x_1\, d\mu_1 + x_2\, d\mu_2 = 0 \tag{1.14.24}$$

which is known as the **Gibbs-Duhem equation**. The Gibbs-Duhem has many uses, as we will see in our discussion of solutions. As an example, suppose we are told that the chemical potential of one of the solution components, say μ_2 depends on its mole fraction x_2 as follows:

$$\mu_2 = \mu_2^* + RT \ln x_2 \tag{1.14.25}$$

where μ_2^* is the chemical potential of pure sample of component 2. Then, using the Gibbs-Duhem relation, we can derive the corresponding dependence of μ_1 on the solution composition. From the Gibbs-Duhem equation,

$$\mu_1 = -\frac{x_2}{x_1} d\mu_2 = -RT \frac{x_2}{x_1} d \ln x_2 = -RT \frac{dx_2}{x_1} \tag{1.14.26}$$

However, a change dx_2 in the number of moles of substance 2 must be equal and opposite to the change in dx_1 in component 1, i.e., $dx_2 = -dx_1$. Therefore,

$$d\mu_1 = RT \frac{dx_1}{x_1} \tag{1.14.27}$$

Integrating this, we find

$$\mu_1 = RT \ln x_1 + C \tag{1.14.28}$$

where the integration constant C can be determined from the condition $x_1 = 1$, corresponding to a pure sample of component 1. When $x_1 = 1$, $\mu_1 = \mu_1^* = C$. Hence,

$$\mu_1 = \mu_1^* + RT \ln x_1 \tag{1.14.29}$$

Solution-Vapor Equilibria

Suppose a two-component solution is in equilibrium with its vapor. Let $n_j^{(\text{soln})}$ and $n_j^{(\text{vap})}$, $j = 1, 2$ denote the number of moles of each component in solution and in vapor, respectively. For concreteness, let component 1 be the major or solvent component. The

Gibbs free energy is a function of the number of moles of each component in solution and in vapor and, of course, P and T:

$$G = G(n_1^{(\text{soln})}, n_2^{(\text{soln})}, n_1^{(\text{vap})}, n_2^{(\text{vap})}, P, T) \tag{1.14.30}$$

Moreover,

$$\begin{aligned} &G(n_1^{(\text{soln})}, n_2^{(\text{soln})}, n_1^{(\text{vap})}, n_2^{(\text{vap})}, P, T) \\ &= G^{(\text{soln})}(n_1^{(\text{soln})}, n_2^{(\text{soln})}, P, T) + G^{(\text{vap})}(n_1^{(\text{vap})}, n_2^{(\text{vap})}, P, T) \end{aligned} \tag{1.14.31}$$

If P and T are held fixed, then

$$dG = \sum_{j=1}^{2} \left[\left(\frac{\partial G^{(\text{soln})}}{\partial n_j^{(\text{soln})}} \right)_{P,T} dn_j^{(\text{soln})} + \left(\frac{\partial G^{(\text{vap}}}{\partial n_J^{(\text{vap})}} \right)_{P,T} dn_j^{(\text{vap})} \right] \tag{1.14.32}$$

However, $dn_j^{(\text{vap})} = -dn_j^{(\text{soln})}$. Thus, in much the same way that we analyzed phase equilibria, we have

$$dG = \sum_{j=1}^{2} \left[\mu_j^{(\text{soln})} dn_j^{(\text{soln})} + \mu_j^{(\text{vap})} dn_j^{(\text{vap})} \right] = \sum_{j=1}^{2} \left[\left(\mu_j^{(\text{vap})} - \mu_j^{(\text{soln})} \right) dn_j^{(\text{vap})} \right] \tag{1.14.33}$$

In equilibrium, $dG = 0$, hence, $\mu_j^{(\text{vap})} = \mu_j^{(\text{soln})}$. Let the vapor phase be treated as an ideal gas with two components. From Dalton's law of partial pressures, the total pressure P in the vapor phase is the sum of partial pressures of each of the individual components coming from the solution $P = \Sigma_j P_j$. For simplicity, suppose we have a two-component solution, which gives rise to two components in the vapor phase. Then $P = P_1 + P_2$. From the ideal gas laws for each component

$$P_1 = \frac{n_1^{(\text{vap})} RT}{V}, \qquad P_2 = \frac{n_2^{(\text{vap})} RT}{V} \tag{1.14.34}$$

where V is the volume of the vapor phase, and T is the temperature. These can be written as

$$P_1 = \frac{n_1^{(\text{vap})}}{n^{(\text{vap})}} \frac{n^{(\text{vap})} RT}{V}, \qquad P_2 = \frac{n_2^{(\text{vap})}}{n^{(\text{vap})}} \frac{n^{(\text{vap})} RT}{V} \tag{1.14.35}$$

where $n^{(\text{vap})} RT/V = P$ is the total pressure. Thus,

$$P_1 = x_1^{(\text{vap})} P, \qquad P_2 = x_2^{(\text{vap})} P \tag{1.14.36}$$

Here, $x_1^{(\text{vap})}$ and $x_2^{(\text{vap})}$ are the vapor-phase mole fractions.

The definition of an ideal solution is one in which

$$x_1^{(\text{vap})} = x_1^{(\text{soln})} \equiv x_1 \tag{1.14.37}$$

meaning that the mole fractions in solution and vapor phases are the same, and we can simply denote the mole fraction of component 1 as x_1. Thus, the partial pressure of component 1 becomes

$$P_1 = x_1 P \tag{1.14.38}$$

When $x_1 = 1$, we have a pure system consisting of component 1, and $P_1 = P = P_1^*$, which denotes the vapor pressure of the pure component 1. Thus, the partial pressure P_1 for the solution becomes

$$P_1 = x_1 P_1^* \tag{1.14.39}$$

which is known as *Raoult's Law*, and it defines an ideal solution.

When $x_1 = 1$, clearly, $P_1 = P_1^*$ (shown as P_1^o in the figure below). The plot below shows how P_1 depends on x_1, which, of course, is a linear plot with slope P_1^* and zero intercept. Any solution that obeys Raoult's law is called an *ideal solution*.

Figure 15.11 also shows how deviations from ideal solution behavior appears. Negative deviations, $P_1 < x_1 P_1^*$, occur when there are strong attractive forces between the components. An example of a solution that would show negative deviations from Raoult's law would be a mixture of trichloromethane ($CHCl_3$) and ethoxyethane ($C_2H_5OC_2H_5$).

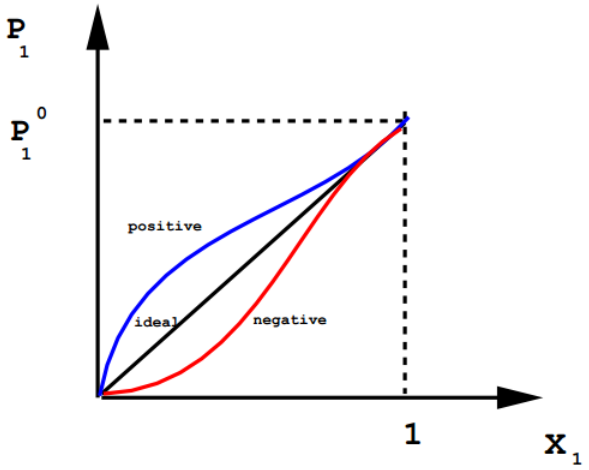


Figure 15.11: Illustration of Raoult's law and deviations from it.

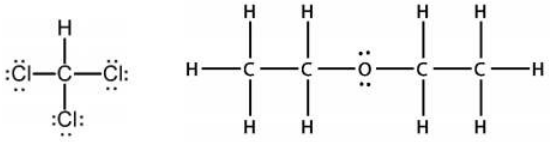


Figure 15.12: Left: Trichloromethane (chloroform). Right: Ethoxyethane.

Trichloromethane has a polar hydrogen but no H-bond acceptor sites (the chlorines are not sufficiently electronegative). Hence, a pure liquid of trichloromethane cannot form hydrogen bonds. However, ethoxyethane has an oxygen with lone pairs. However, when it is mixed with trichloromethane, hydrogen bonds can form. these are strong attractive interactions that cause negative deviations from Raoult's law.

Positive deviations from Raoult's law ($P_1 > x_1 P_1^*$) arise when there are strong repulsive forces between the components. Alcohol-water mixtures (e.g. ethanol-water or methanol-water) are examples of solutions that show positive deviations from Raoult's law. In order to see why a methanol-water solution exhibits a positive deviation, consider the computer simulation snapshots of such a solution with $x_1 = x_2 = 0.5$, shown in the figure below. A solution of this type fill show positive deviations from Raoult's law.

Most solutions show deviations from ideal solution behavior. However, Raoult's law nevertheless still provides a number of important insights. In the first place, as $x_1 \to 1$, $P_1 \to P_1^*$ because this corresponds to the case of just one component. Near $x_1 = 1$, all solutions behave ideally, just as all gases tend to ideal gas behavior as the density approaches zero. This is exactly what Figure 15.11 shows. For $x_1 \lesssim 1$, $P_1 = x_1 P_1^*$, and Raoult's law holds.

Away from $x_1 \lesssim 1$, deviations are expected, and P_1 does not vary linearly with x_1. However, looking at Figure 15.11, we see that as $x_1 \to 0$, P_1 varies linearly with x_1, however, the slope is not P_1^* any more. We express this linear relation as

$$P_1 = k_{H,1} x_1 \tag{1.14.40}$$

which is called *Henry's Law*. The constant $k_{H,1}$ is called the Henry's law constant, and it clearly has units of pressure. If $k_{H,1} = P_1^*$, then the solution is an ideal solution. The degree to which $k_{H,1}$ differs from P_1^* is a measure of non-ideality of the solution.

Interestingly, the shape of the P_1 vs x_1 curve can be fit accurately to a function of the following form

$$P_1(x_1) = P_1^* x_1 e^{b(1-x_1)^2 + c(1-x_1)^3} \tag{1.14.41}$$

Positive deviations from Raoult's law can be described by $b > 0$ and $c > 0$, while negative deviations can be described by $b < 0$ and $c < 0$. The figure below shows a plot of Equation 15.31 for several choices of b and c.

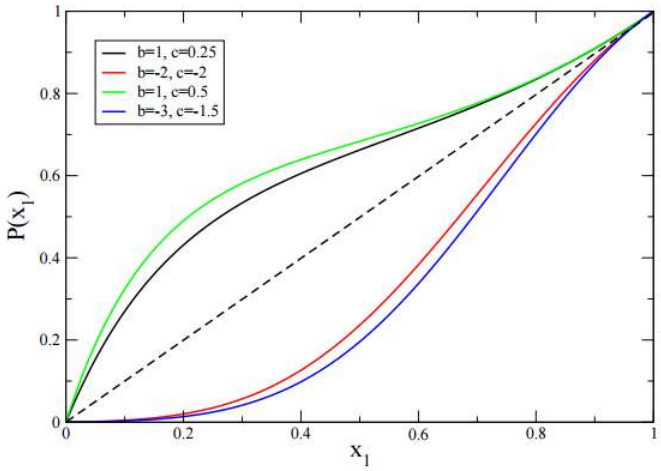


Figure 15.13: Plot of Equation 15.31 for several choices of parameters showing positive and negative deviations.

Example 1.14.1

Suppose we are told that P_1^* torr, $b = 1$, and $c = 0.5$. What is the Henry's law constant for this model?

Solution

For x_1 very small, we can work to linear order in Equation 15.31. To linear order, we find

$$P_1(x_1) \approx P_1^* x_1 e^{1+0.5} = P_1^* x_1 e^{1.5} \tag{1.14.42}$$

from which we can read off the Henry's law constant as

$$k_{H,1} = P_1^* e^{1.5} = (180 \text{ torr}) e^{1.5} = 807 \text{ torr} \tag{1.14.43}$$

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1.15: Solution Equilibria and Colligative Properties

Statistical Mechanics of Solvation: Solvation Free Energies

We consider a solvent with coordinates $\mathbf{r}_1^{(a)}, \ldots, \mathbf{r}_{N_a}^{(a)}$ in to which a solute with coordinates $\mathbf{r}_1^{(b)}, \ldots, \mathbf{r}_{N_b}^{(b)}$. The total number of particles in the system is $N = N_a + N_b$. Let $\mathbf{r}^{(a)}$ denote the full set of solvent coordinates, $\mathbf{r}^{(b)}$ denote the full set of solute coordinates, and $\mathbf{r} = (\mathbf{r}^{(a)}, \mathbf{r}^{(b)})$ denote the full set of coordinates in the system. The pure system of each system, before the solute is introduced into the solvent, is described by a potential energy

$$U^*(\mathbf{r}) = U_a(\mathbf{r}^{(a)}) + U_b(\mathbf{r}^{(b)}) \tag{1.15.1}$$

When the solute is introduced into the solvent, we change the thermodynamic state of the system, and we change the mechanical state as well. Hence, the potential energy for the solution is of the form

$$U(\mathbf{r}) = U^*(\mathbf{r}) + U_{ab}(\mathbf{r}^{(a)}, \mathbf{r}^{(b)}) \tag{1.15.2}$$

where U_{ab} is an interaction potential between solvent and solute, which we can take to be a pair potential

$$U_{ab}(\mathbf{r}^{(a)}, \mathbf{r}^{(b)}) = \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} u_{ab}\left(\left|\mathbf{r}_1^{(a)} - \mathbf{r}_j^{(b)}\right|\right) \tag{1.15.3}$$

In order to affect the change of thermodynamic state so that we can compute the solvation free energy, we define an arbitrary path via the introduction of a coupling parameter λ that slowly, reversibly switches on the interaction between solvent and solute:

$$\tilde{U}(\mathbf{r}; \lambda) = (1 - \lambda) U^*(\mathbf{r}) + \lambda U(\mathbf{r}) \tag{1.15.4}$$

Note that $\tilde{U}(\mathbf{r};, 0) = U^*(\mathbf{r})$ is the potential of the pure substances, and $\tilde{U}(\mathbf{r}, 1) = U(\mathbf{r})$ is the potential energy for the solution. Here $\lambda \in [0, 1]$ is a continuous parameter that we slowly switch from 0 to 1, thereby slowly solvating the solute in the solvent.

Let $A(\lambda)$ denote the Helmholtz free energy for $\tilde{U}(\mathbf{r};, \lambda)$ at a particular value of λ. The solvation Helmholtz free energy is then given by the relation

$$\Delta_{\text{solv}} A = A(1) - A(0) = \int_0^1 \frac{dA}{d\lambda} d\lambda \tag{1.15.5}$$

Note that

$$A(\lambda) = -\frac{1}{\beta} \ln Z(\lambda) \tag{1.15.6}$$

$$Z(\lambda) = \int d\mathbf{r}\, e^{-\beta \tilde{U}(\mathbf{r}; \lambda)} \tag{1.15.7}$$

$$\frac{dA}{d\lambda} = -\frac{1}{\beta Z(\lambda)} \frac{dZ}{d\lambda} \tag{1.15.8}$$

$$= \frac{1}{Z(\lambda)} \int d\mathbf{r}\, \frac{\partial \tilde{U}}{\partial \lambda} e^{-\beta \tilde{U}(\mathbf{r}; \lambda)} \tag{1.15.9}$$

But

$$\frac{\partial \tilde{U}}{\partial \lambda} = -U^*(\mathbf{r}) + U^*(\mathbf{r}) + U_{ab}(\mathbf{r}^{(a)}, \mathbf{r}^{(b)}) = U_{ab}(\mathbf{r}^{(a)}, \mathbf{r}^{(b)}) \tag{1.15.10}$$

Therefore,

$$\frac{dA}{d\lambda} = \frac{1}{Z(\lambda)} \int d\mathbf{r}\, U_{ab}(\mathbf{r}^{(a)}, \mathbf{r}^{(b)}) e^{-\beta \tilde{U}(\mathbf{r}; \lambda)} \tag{1.15.11}$$

Now, define the radial distribution function at a given value of λ as

$$\tilde{g}_{ab}(r; \lambda) = \frac{N_a V}{\rho_a Z(\lambda)} \int_{|\mathbf{r}_1^{(a)} - \mathbf{r}_1^{(b)}| = r} d\mathbf{r}\, e^{-\beta \tilde{U}(\mathbf{r}; \lambda)} \tag{1.15.12}$$

Then

$$\frac{dA}{d\lambda} = \frac{1}{Z(\lambda)} N_a N_b \int d\mathbf{r}\, u_{ab}\left(\left|\mathbf{r}_1^{(a)} - \mathbf{r}_1^{(b)}\right|\right) e^{-\beta\tilde{U}(\mathbf{r};\lambda)} \tag{1.15.13}$$

$$= N_b \int d\mathbf{r}_1^{(a)} d\mathbf{r}_1^{(b)} u_{ab}\left(\left|\mathbf{r}_1^{(a)} - \mathbf{r}_1^{(b)}\right|\right) \left[\frac{N_a}{Z(\lambda)} \int d\mathbf{r}'\, e^{-\beta\tilde{U}(\mathbf{r};\lambda)}\right] \tag{1.15.14}$$

$$= N_b \int d\mathbf{R}\, d\mathbf{r}\, u_{ab}(|\mathbf{r}|) \left[\frac{N_a}{Z(\lambda)} \int d\mathbf{r}'\, e^{-\beta\tilde{U}(\mathbf{r};\lambda)}\right] \tag{1.15.15}$$

$$= 4\pi N_b V \int_0^\infty dr\, r^2\, u_{ab}(r) \left[\frac{N_a}{Z(\lambda)} \int d\mathbf{r}'\, e^{-\beta\tilde{U}(\mathbf{r};\lambda)}\right] \tag{1.15.16}$$

$$= 4\pi N_b \rho_a \int_0^\infty dr\, r^2\, u_{ab}(r) \left[\frac{N_a V}{\rho_a Z(\lambda)} \int_{|\mathbf{r}|=r} d\mathbf{r}\, e^{-\beta\tilde{U}(\mathbf{r};\lambda)}\right] \tag{1.15.17}$$

$$= 4\pi N_b \rho_a \int_0^\infty dr\, r^2\, u_{ab}(r)\, \tilde{g}_{ab}(r;\lambda) \tag{1.15.18}$$

We now integrate over $\boldsymbol{\lambda}$ to obtain the solvation free energy

$$\Delta_{\text{solv}} A = 4\pi N_b \rho_a \int_0^\infty dr\, r^2\, u_{ab}(r) \int_0^1 d\lambda\, \tilde{g}_{ab}(r;\lambda) \tag{1.15.19}$$

Now define

$$g_{ab}(r) = \int_0^1 d\lambda\, \tilde{g}_{ab}(r;\lambda) \tag{1.15.20}$$

which is the solvation radial distribution function and measures the work to bring together solute and solvent particles at a distance r from each other. Then,

$$\Delta_{\text{solv}} A = 4\pi N_b \rho_a \int_0^\infty dr\, r^2\, u_{ab}(r)\, g_{ab}(r) \tag{1.15.21}$$

Now, we compute the solvation chemical potential as the solvation free energy per solute particle

$$\Delta_{\text{solv}} \mu = \frac{\partial \Delta_{\text{solv}} A}{\partial N_b} = 4\pi \rho_a \int_0^\infty dr\, r^2\, u_{ab}(r)\, g_{ab}(r) \tag{1.15.22}$$

Finally, then, the molar solvation free energy is simply obtained by multiplying this by Avogadro's number N_A:

$$\Delta_{\text{solv}} \mu = \frac{\partial \Delta_{\text{solv}} A}{\partial N_b} = 4\pi \rho N_A \int_0^\infty dr\, r^2\, u_{ab}(r)\, g_{ab}(r) \tag{1.15.23}$$

Chemical Potentials in Solution-Vapor Equilibria

When treating the vapor as an ideal gas, it is relevant to ask what the Gibbs free energy of the vapor phase, and therefore, the chemical potential are. Recall that the partition function of an ideal gas of just one component is

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \tag{1.15.24}$$

where $\lambda = \sqrt{\beta h^2/2\pi m}$. The Gibbs free energy, however, comes from the isobaric partition function $\Delta(N,P,T)$, given by

$$\Delta(N,P,T) = \int_0^\infty dV\, e^{-\beta PV} Q(N,V,T) \tag{1.15.25}$$

$$= \frac{1}{N!\lambda^{3N}} \int_0^\infty e^{-\beta PV} V^N dV \tag{1.15.26}$$

$$= \frac{1}{(\beta P)^{N+1}\lambda^{3N}} \tag{1.15.27}$$

$$\approx \frac{1}{(\beta P)^N \lambda^{3N}} \tag{1.15.28}$$

Therefore, the Gibbs free energy is

$$G(N,P,T) = -\frac{1}{\beta}\ln \Delta(N,P,T)$$
$$= N\,\mathrm{K}\cdot\mathrm{kg}\cdot\mathrm{mol}^{-1}\,T\ln\beta + N\,\mathrm{K}\cdot\mathrm{kg}\cdot\mathrm{mol}^{-1}\,T\ln P + 3N\,\mathrm{K}\cdot\mathrm{kg}\cdot\mathrm{mol}^{-1}\,T\ln\lambda$$

Now suppose we have a process in which we change P_1 to P_2 in a gas at fixed N and T. The change in Gibbs free energy is

$$\Delta G = G(N,P_2,T) - G(N,P_1,T) = N\,\mathrm{K}\cdot\mathrm{kg}\cdot\mathrm{mol}^{-1}\,T\ln\left(\frac{P_2}{P_1}\right) = nRT\ln\left(\frac{P_2}{P_1}\right)$$

Thus, the molar Gibbs free energy is

$$\Delta\tilde{G} = \frac{\Delta G}{n} = \mu = RT\ln\left(\frac{P_2}{P_1}\right)$$

which is also the chemical potential of the gas.

In thermodynamics, we can only define changes relative to an arbitrary reference, so we actually need to define that reference. This reference is known as the *standard state*. For gases, the standard state is a pressure of $1\ \mathrm{atm}$ at some specified temperature, assuming ideal-gas behavior, i.e., that $PV = nRT$. The pressure of the standard state is denoted P°, and it is just a constant having the value of $1\ \mathrm{atm}$. If we now consider a change from the standard state to an arbitrary pressure P, the change in the Gibbs free energy is then given by

$$\Delta\tilde{G} = \Delta\tilde{G}^{\circ}(T) + RT\ln\left(\frac{P}{P^{\circ}}\right)$$

and the chemical potential, which is the same thing, is

$$\mu = \mu^{\circ}(T) + RT\ln\left(\frac{P}{P^{\circ}}\right)$$

Let us denote a general component in our system as j, i.e., $j = A, B$ in a two-component solution. For each component in the vapor phase,

$$\mu_j^{(\mathrm{vap})} = \mu_j^{\circ} + RT\ln\left(\frac{P_j}{P_j^{\circ}}\right) \tag{1.15.29}$$

However, in equilibrium $\mu_j^{(\mathrm{vap})} = \mu_j^{(\mathrm{soln})}$. Therefore, if we take $P_j^{\circ} = 1\ \mathrm{atm}$, then

$$\mu_j^{(\mathrm{vap})} = \mu_j^{(\mathrm{soln})} = \mu_h^{\circ} + RT\ln P_j \tag{1.15.30}$$

An equivalent expression for a pure sample of component j in an equilibrium between its liquid and vapor would appear as

$$\mu_j^{*}(\mathrm{liquid}) = \mu_j^{*}(\mathrm{vapor}) = \mu_j^{\circ} + RT\ln P_j^{*} \tag{1.15.31}$$

Subtracting the two expressions yields

$$\mu_j^{(\mathrm{soln})} = \mu_j^{*}(\mathrm{liquid}) + RT\ln\left(\frac{P_j}{P_j^{*}}\right) \tag{1.15.32}$$

Moreover,

$$\begin{aligned}\mu_j^{(\mathrm{soln})} &= \mu_j^{(\mathrm{vap})} = \mu_j^{\circ} + RT\ln(x_j P)\\ &= \mu_j^{\circ} + RT\ln x_j + RT\ln P\end{aligned} \tag{1.15.33}$$

Thus, for each of the two components,

$$\mu_1^{(\mathrm{soln})} = \mu_1^{(\mathrm{vap})} = \mu_1^{\circ} + RT\ln x_1 + RT\ln P \tag{1.15.34}$$
$$\mu_2^{(\mathrm{soln})} = \mu_2^{(\mathrm{vap})} = \mu_2^{\circ} + RT\ln x_2 + RT\ln P \tag{1.15.35}$$
$$\mu_2^{(\mathrm{soln})} - \mu_1^{(\mathrm{soln})} = \mu_2^{\circ} - \mu_1^{\circ} + RT\ln\left(\frac{x_2}{x_1}\right) \tag{1.15.36}$$

This shows that the difference of chemical potentials of the two components in solution is related to the logarithms of the ration of the mole fractions. Due to the equilibrium condition

$$\mu_2^{(vap)} - \mu_1^{(vap)} = \mu_2^{\circ} - \mu_1^{\circ} + RT \ln \left(\frac{x_2}{x_1} \right) \tag{1.15.37}$$

which relates the chemical potential difference to the same mole fraction ratio (which we recall is the ratio of gas-phase mole fractions); the same mole fraction ratio must be the same in solution in order to determine the solution-phase chemical potential difference.

Non-Ideal Solutions and Activities

We showed that the solution chemical potential is

$$\mu_j^{(soln)} = \mu_j^*(\text{liquid}) + RT \ln \left(\frac{P_j}{P_j^*} \right) \tag{1.15.38}$$

In an ideal solution $P_j = x_j P_j^*$, in which case

$$\mu_j^{(soln)} = \mu_j^*(\text{liquid}) + RT \ln x_j \tag{1.15.39}$$

In a non-ideal solution, we can fit the behavior of P_1 vs. x_1 as

$$P_1 = x_1 P_1^* e^{b(1-x_1)^2 + c(1-x_1)^3} \tag{1.15.40}$$

and

$$\mu_1^{(soln)} = \mu_1^*(\text{liquid}) + RT \ln x_1 + RTb(1-x_1)^2 + RTc(1-x_1)^3 \tag{1.15.41}$$

The second and third and fourth terms on the right of this expression measure the deviation from ideal behavior, and we see that as $x_1 \to 1$,

$$\mu_1^{(soln)} \to \mu_1^*(\text{liquid}) + RT \ln x_1 \tag{1.15.42}$$

Let us define

$$a_j = \frac{P_j}{P_j^*} \tag{1.15.43}$$

which is called the *activity*. For an ideal solution, $a_j = x_j$. Generally, however, $P_j / P_j^* \neq x_j$ but is rather some function $f(x_1)$ of x_1. Thus, in the non-ideal case, we can write

$$\mu_j^{(soln)} = \mu_j^*(\text{liquid}) + RT \ln a_j \tag{1.15.44}$$

The ratio

$$\gamma_j = \frac{a_j}{x_j} \tag{1.15.45}$$

is known as the *activity coefficient* and is equal to 1 for ideal solutions. Activities can be defined for any state of a substance, i.e., solutions, dissolved species, gases, liquids, solids,...

Characterizing Solid-Liquid Solutions and Dissolved Species

Solid-liquid solutions involved the dissolution of a solid substance in a solvent leading to a homogeneous mixture. We will discuss the microscopic nature of dissolved species later in the lecture. Before we get into that, however, let us discuss some basic measures for characterizing the composition of such a solution.

The most common measure of solution composition is the *molarity* defined as

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solvent}} \tag{1.15.46}$$

and is denoted M. A second measure is known as the *molality* defined as

$$\text{molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}} \tag{1.15.47}$$

Example 1.15.1:

A solution has a solvent (component 1) and $N-1$ dissolved species indexed $k = 2, \ldots, N$. Let x_1 be the mole fraction of the solvent and $x_2, \ldots, x_N$ be the mole fractions of each of the dissolved solute species. Let M_1 be the molar mass of the solvent. Show that

$$x_1 = \frac{1}{1 + \dfrac{M_1 m}{1000}}, \qquad x_k = \frac{M_1 m_k / 1000}{1 + \dfrac{M_1 m}{1000}} \tag{1.15.48}$$

where m_k is the molality of the k^{th} component and m is the total molality of the solution, i.e.,

$$m_k = \frac{\text{moles of component } k}{\text{kilograms of solvent}}, \qquad m = \sum_{k=2}^{N} m_k \tag{1.15.49}$$

Solution

Start with the definition of the mole fractions. For component, the definition is

$$x_1 = \frac{n_1}{n_1 + \Sigma_{k=2}^{N} n_k}$$

Divide top and bottom by n_1 to give

$$x_1 = \frac{1}{1 + \Sigma_{k=2}^{N} \dfrac{n_k}{n_1}}$$

The number of moles of solvent is

$$n_1 = \frac{\text{mass of solvent in grams}}{M_1} \tag{1.15.50}$$

$$= \frac{1000(\text{mass of solvent in kilograms})}{M_1} \tag{1.15.51}$$

$$= \frac{1000 \mu_1}{M_1} \tag{1.15.52}$$

where μ_1 is the mass of solvent in kilograms. Thus, x_1 becomes

$$x_1 = \frac{1}{1 + \dfrac{M_1}{1000} \sum_{k=2}^{N} \dfrac{n_k}{\mu_1}} \tag{1.15.53}$$

$$= \frac{1}{1 + \dfrac{M_1 m}{1000}} \tag{1.15.54}$$

where n_k/μ_1 is the molality of component k, and $m = \Sigma_{k=2}^{N} m_k$. For component k,

$$n_k = \frac{n_k}{n_1 + \sum_{j=2}^{N} n_j} = \frac{n_k/n_1}{1 + \sum_{j=2}^{N} \dfrac{n_j}{n_1}}$$

Use the fact that $n_1 = 1000\mu_1/M_1$. Substituting this in, we obtain

$$n_k = \frac{\dfrac{M_1}{1000} \dfrac{n_k}{\mu_1}}{1 + \dfrac{M_1}{1000} \sum_{j=2}^{N} \dfrac{n_j}{\mu_1}}$$

Again, since $n_j/\mu_1 = m_j$, and $m = \Sigma_{j=2}^{N} m_j$, we finally obtain

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$$x_k = \frac{M_1 m_k / 1000}{1 + \frac{M_1 m}{1000}}$$

Example 1.15.2:

A solution is prepared by dissolving $22.4\ \text{g}$ of $MgCl_2$ in $0.2\ \text{L}$ of water. The resulting solution has a density of $1.098\ \text{g/cm}^3$. Calculate the mole fraction, molarity, and molality of $MgCl_2$ in the solution.

Solution

The molar mass of $MgCl_2$ is $95.22\ \text{g/mol}$. Thus, the moles of $MgCl_2$ are

$$\text{moles of } MgCl_2 = \frac{22.4\ \text{g}}{95.22\ \text{g/mol}} = 0.235\ \text{moles}$$

In addition

$$\text{mass of water} = (0.2\ \text{L})\left(\frac{1000\ \text{cm}^3}{1.0\ \text{L}}\right)(1.00\ \text{g/cm}^3) = 200\ \text{g}$$

The molar mass of water is $18.02\ \text{g/mol}$. Hence, the moles of water are

$$\text{moles of water} = \frac{200\ \text{g}}{18.02\ \text{g/mol}} = 11.1\ \text{moles}$$

The mole fraction of $MgCl_2$, which is component 2, becomes

$$x_2 = \frac{0.235\ \text{moles}}{(11.1 + 0.235)\ \text{moles}} = 0.0207\ \text{moles}$$

The total solution volume is

$$\text{solution volume} = \frac{\text{mass of solution}}{\text{density of solution}} \tag{1.15.55}$$

$$= \frac{22.4\ \text{g} + 200\ \text{g}}{1.098\ \text{g/cm}^3} \tag{1.15.56}$$

$$= 204\ \text{cm}^3 \tag{1.15.57}$$

$$= 0.204\ \text{L} \tag{1.15.58}$$

Thus, the molarity of $MgCl_2$ is

$$\text{Molarity} = \frac{0.235\ \text{moles}}{0.204\ \text{L}} = 1.15\ \text{M}$$

Finally, the molality is

$$\text{molality} = \frac{0.235\ \text{moles}}{0.2\ \text{kg}} = 1.18\ \text{mol/kg} = 1.18\ \text{m}$$

Freezing Point Depression

At the freezing point, the solid solvent is in equilibrium with the liquid solvent. This requires

$$\mu_1^{(\text{solid, soln})}(P,T) = \mu_1^{(\text{liq, soln})}(P,T) \tag{1.15.59}$$

where component 1 is the solvent. Recall, however, that

$$\mu_1^{(\text{liq, soln})} = \mu_1^*(\text{pure liquid}) + RT \ln a_1 = \mu_1^{(\text{solid, soln})} \tag{1.15.60}$$

Thus,

$$\ln a_1 = \frac{\mu_1^{(\text{solid, soln})} - \mu_1^*(\text{pure liquid})}{RT} \tag{1.15.61}$$

How does a_1 depend on T? Take the temperature derivative of both sides:

$$\frac{\partial \ln a_1}{\partial T} = \frac{1}{R}\left[\frac{\partial(\mu_1^{(\text{solid, soln})}/T)}{\partial T} - \frac{\partial(\mu_1^*(\text{pure liquid})/T)}{\partial T}\right] \tag{1.15.62}$$

For a general chemical potential, use the fact that $G(n,P,T) = \mu(P,T) = H - TS$,

$$\frac{G}{T} = \frac{H}{T} - S = \frac{\mu}{T}n \tag{1.15.63}$$

$$\frac{\partial(G/T)}{\partial T} = \mu\,\partial(\mu/T)/\partial T = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right) - \frac{\partial S}{\partial T} \tag{1.15.64}$$

However, remember that

$$\frac{\partial H}{\partial T} = C_P(T) \tag{1.15.65}$$

and, under isobaric conditions,

$$S = \int \frac{dQ_{\text{rev}}}{T} \tag{1.15.66}$$

$$= \int \frac{dH}{T} \tag{1.15.67}$$

$$= \int \frac{C_P(T)\,dT}{T} \tag{1.15.68}$$

$$dS = \frac{C_P(T)\,dT}{T} \tag{1.15.69}$$

$$\frac{\partial S}{\partial T} = \frac{C_P(T)}{T} \tag{1.15.70}$$

Therefore,

$$\frac{\partial(G/T)}{\partial T} = n\partial(\mu/T)/\partial T = -\frac{H}{T^2} + \frac{C_P(T)}{T} - \frac{C_P}{T} \tag{1.15.71}$$

$$= -\frac{H}{T^2} \tag{1.15.72}$$

Applying Equation 16.42 to the molar Gibbs free energy μ, we obtain

$$\frac{\partial(\mu/T)}{\partial T} = -\frac{\tilde{H}}{T^2} \tag{1.15.73}$$

where $\tilde{H}$ is the molar enthalpy. Thus, for the solvent

$$\frac{\partial(\mu_1/T)}{\partial T} = -\frac{\tilde{H}_1}{T^2} \tag{1.15.74}$$

We can use these results to determine the activity and ultimately the amount of freezing point depression. If we differentiate Equation 16.37 with respect to temperature and apply the above result, we obtain

$$\frac{\partial \ln a_1}{\partial T} = \frac{1}{R}\left[\frac{\partial(\mu_1^{(\text{solid, soln})}/T)}{\partial T} - \frac{\partial(\mu_1^*(\text{pure liq})/T)}{\partial T}\right] \tag{1.15.75}$$

$$= -\frac{\tilde{H}_1^{(\text{solid, soln})} - \tilde{H}_1^*(\text{pure liq})}{RT^2} \tag{1.15.76}$$

$$= \frac{\tilde{H}_1(\text{pure liq}) - \tilde{H}_1^{(\text{solid, soln})}}{RT^2} \tag{1.15.77}$$

Now we assume that, in a dilute solution, the solvent dominates, so that $\tilde{H}_1^*(\text{pure liq}) \approx \tilde{H}_1^{(\text{liquid, soln})}$. Thus,

$$\frac{\partial \ln a_1}{\partial T} = \frac{\tilde{H}_1^{\text{(liquid, soln)}} - \tilde{H}^{\text{(solid, soln)}}}{RT^2} \tag{1.15.78}$$

$$= \frac{\Delta_{\text{fus}} \tilde{H}_1}{RT^2} \tag{1.15.79}$$

In order to see if there is a change in the freezing point, we need to integrate both sides from T^*_{fus}, the freezing point of the pure solvent, to T_{fus}, the freezing point of the solution. This gives

$$\ln a_1 = \int_{T^*_{\text{fus}}}^{T_{\text{fus}}} \frac{\Delta_{\text{fus}} \tilde{H}_1}{RT^2} dT \tag{1.15.80}$$

Let us assume that the solution is dilute so that $a_1 \approx x_1$, $\ln a_1 \approx \ln x_1 = \ln(1 - x_2) \approx -x_2$, where $x_2 \ll 1$. We then have

$$-x_2 = -\frac{\Delta_{\text{fus}} \tilde{H}_1}{RT} \Bigg|_{T^*_{\text{fus}}}^{T_{\text{fus}}} \tag{1.15.81}$$

$$= \frac{\Delta_{\text{fus}} \tilde{H}_1}{R} \left[\frac{1}{T^*_{\text{fus}}} - \frac{1}{T_{\text{fus}}} \right] \tag{1.15.82}$$

$$-x_2 \approx \frac{\Delta_{\text{fus}} \tilde{H}_1}{R} \left[\frac{T_{\text{fus}} - T^*_{\text{fus}}}{T_{\text{fus}} T^*_{\text{fus}}} \right] \tag{1.15.83}$$

Since $\Delta \tilde{H}_{\text{fus}} > 0$, it follows that $T_{\text{fus}} < T^*_{\text{fus}}$, hence, for the solution, the freezing point is lowered.

Previously, we showed that

$$x_2 = \frac{M_1 m_2 / 1000}{1 + M_1 m / 1000} \tag{1.15.84}$$

For a two-component solution $m_2 = m$, hence this becomes

$$x_2 = \frac{M_1 m / 1000}{1 + M_1 m / 1000} \tag{1.15.85}$$

which we can write as

$$x_2 = \frac{m}{m + \dfrac{1000}{M_1}} \tag{1.15.86}$$

$$\approx \frac{m}{1000 / M_1} \tag{1.15.87}$$

$$= \frac{M_1 m}{1000} \tag{1.15.88}$$

where we have assumed that $m \ll 1000 / M_1$. Now, let $\Delta T_{\text{fus}} = T^*_{\text{fus}} - T_{\text{fus}}$. Hence, we can write

$$x_2 = \frac{\Delta_{\text{fus}} \tilde{H}_1}{R} \frac{\Delta T_{\text{fus}}}{T_{\text{fus}} T^*_{\text{fus}}} \approx \frac{M_1 m}{1000} \tag{1.15.89}$$

Solving for the change in the freezing temperature ΔT_{fus}, we obtain

$$\Delta T_{\text{fus}} \approx \frac{T_{\text{fus}} T^*_{\text{fus}} R}{\Delta_{\text{fus}} \tilde{H}_1} \frac{M_1}{1000} m \equiv K_f m \tag{1.15.90}$$

where K_f is a constant known as the freezing-point depression constant.

By a similar argument, it can also be shown that the boiling point of the solution is elevated, i.e.,

$$\Delta T_{\text{vap}} = K_b m \tag{1.15.91}$$

Boiling point elevation and freezing point depression can be used to determine molar masses. The following examples illustrate how this is done:

Example 1.15.3

When $5.50\ \text{g}$ of biphenyl ($C_{12}H_{10}$) is dissolved in $100.0\ \text{g}$ of benzene, the boiling point increases by $0.903°C$. When $6.3\ \text{g}$ of an unknown hydrocarbon is dissolved in $150.0\ \text{g}$ of benzene, the boiling point of the solution increases by $0.597°C$. What is the molar mass of the solute?

Solution

$$\text{moles of biphenyl} = \frac{5.5\ \text{g}}{154.2\ \text{g/mol}} = 0.0357\ \text{mol}$$

$$\text{molality of solution} = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.0357\ \text{mol}}{0.1\ \text{kg}} = 0.357\ \text{mol/kg}$$

Therefore, we can determine the constant K_b:

$$K_b = \frac{\Delta T_b}{m} = \frac{0.903\ \text{K}}{0.357\ \text{mol/kg}} = 2.53\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

Now that we know the value of K_b for benzene, we can use it to determine the molar mass of the unknown solute. Given the increase in the boiling temperature, we solve for the molality of the unknown solution:

$$m = \frac{\Delta T_b}{K_b} = \frac{0.597\ \text{K}}{2.53\ \text{K} \cdot \text{kg} \cdot \text{mol}^{-1}} = 0.236\ \text{mol/kg}$$

From this, we can determine the number of moles of the solute:

$$\begin{aligned}\text{moles of solute} &= \text{molality of solution} \times \text{kilograms of solvent} \\ &= (0.236\ \text{mol/kg})(0.150\ \text{kg}) = 0.0354\ \text{mol}\end{aligned}$$

Then, given the number of grams of solute, the molar mass is

$$M = \frac{6.3\ \text{g}}{0.0354\ \text{mol}} = 178\ \text{g/mol}$$

Example 1.15.4

When $0.494\ \text{g}$ of $K_3Fe(CN)_6$ is dissolved in $100.0\ \text{g}$ of water, the freezing point is found to be $-0.1116°C$. What is the dissociation reaction for $K_3Fe(CN)_6$? The K_f for water is $1.86\ \text{kg} \cdot \text{K/mol}$.

Solution

We first calculate the molality of the solute:

$$m = \frac{0.1116\ \text{K}}{1.86\ \text{kg} \cdot \text{K/mol}} = 0.06\ \text{mol/kg}$$

Thus, we have

$$(0.06\ \text{mol/kg})(0.1\ \text{kg}) = 0.006\ \text{mol}$$

moles of solute. The molar mass of $K_3Fe(CN)_6$ is $329.25\ \text{g/mol}$. This gives

$$\frac{0.494\ \text{g}}{329.25\ \text{g/mol}} = 0.0015\ \text{mol}$$

of $K_3Fe(CN)_6$. We know, however, that this solute dissociates into ions, and there must be $0.0015 \times 4 = 0.006$ moles of ions in the solution. Accordingly, the dissociation reaction must be

$$K_3Fe(CN)_6 \longrightarrow 3K^+(\text{aq}) + [Fe(CN)_6]^{3-}(\text{aq})$$

which gives 4 moles of ions per 1 mole of undissociated solute.

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1.16: Thermochemistry

In chemical reactions, bonds are broken and reformed, and heat may be given off or taken up in such processes. Since reactions are often carried out at constant pressure, the change in enthalpy is the appropriate measure of heat given off or absorbed.

Enthalpies of Reaction

The overall change in the enthalpy between products and reactants in a reaction is called the *reaction enthalpy*. The reaction enthalpy can be either positive or negative. As an example, consider the reaction:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \tag{1.16.1}$$

The change enthalpy when 1 mol of CO reacts completely with 0.5 mol of O_2 at $25°C$ can be measured by calorimetry and is observed to be

$$\Delta H = H(\text{products}) - H(\text{reactants}) = q_P = -283.0\,\text{kJ} \tag{1.16.2}$$

The negative sign means that heat is given off by the system, rather than absorbed by it.

When heat is given off, the reaction is said to be *exothermic*. and ΔH will be negative. If heat is absorbed, the reaction is said to be *endothermic*:

$$2\,CO_2(g) \longrightarrow 2\,CO(g) + O_2(g) \tag{1.16.3}$$

the enthalpy of the reaction would be

$$\Delta H = 2 \times 283.0\text{kJ} = 566.0\text{kJ} \tag{1.16.4}$$

Example 17.1

Consider the reaction of solid phosphorus with liquid bromine:

$$2\,P(s) + 3\,Br_2(l) \longrightarrow 2\,PBr_3(g) \qquad \Delta H = -243\text{kJ} \tag{1.16.5}$$

Suppose 2.63 g of phosphorus reacts with an excess of bromine. Calculate the enthalpy change.

Solution

Noting that the specified ΔH of -243 kJ refers to a reaction of 2 ml of solid phosphorus, we calculate the number of moles that correspond to 2.63 g:

$$\text{moles of P} = \frac{2.63\text{g}}{30.97\text{g/mol}} = 0.0849\text{mol} \tag{1.16.6}$$

Thus, the enthalpy change when $0,0849$ mol of phosphorus react is

$$\Delta H = 0.0849\text{mol} \times \left(\frac{-243\text{kJ}}{2\text{mol P}}\right) = -10.3\text{kJ} \tag{1.16.7}$$

Hess's Law

Suppose a reaction is carried out in several steps, We have already seen that the *overall reaction* is the algebraic sum of the individual steps. Because energy/enthalpy is an additive quantity, *the overall enthalpy change for the overall reaction, obtained by adding the individual chemical equations, will be the sum of the enthalpy changes associated with each of the individual steps/chemical equations.* This statement is known as Hess's Law.

Hess's Law can be used to calculate the enthalpy of reactions that cannot be carried out straightforwardly in the lab. As an example, consider the reaction of solid carbon, in the form of graphite, with oxygen gas to product carbon monoxide:

$$C(s, gr) + \frac{1}{2}O_2 \longrightarrow CO(g) \tag{1.16.8}$$

This reaction cannot be carried out directly experimentally. Rather, a two-step process is used, in which solid carbon is first converted to carbon *di*oxide via the reaction

$$C(s, gr) + O_2 \longrightarrow CO_2(g) \qquad \Delta H = -393.5\text{kJ} \tag{1.16.9}$$

whose enthalpy can be easily measured at (25^\\text{o}C\). Then the decomposition of CO_2 to give oxygen gas and carbon monoxide can be added to this reaction according to:

$$\begin{aligned} C(s, gr) + O_2 &\longrightarrow CO_2(g) && \Delta H_1 = -393.5\text{kJ} \\ CO_2(g) &\longrightarrow CO(g) + \tfrac{1}{2}O_2 && \Delta H_2 = +283.0\text{kJ} \\ C(s, gr) + \tfrac{1}{2}O_2(g) &\longrightarrow CO(g) && \Delta H_1 + \Delta H_2 = -110.5\text{kJ} \end{aligned} \tag{1.16.10}$$

Example 17.2

Calculate the reaction enthalpy for

$$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s) \tag{1.16.11}$$

given that the follow reaction enthalpies are known:

$$\begin{aligned} &(1) \quad 2\,P(s) + 3\,Cl_2(g) \longrightarrow 2\,PCl_3(l) \quad \Delta_r H^{(1)} = -640\text{kJ} \\ &(2) \quad 2\,P(s) + 5\,Cl_2(g) \longrightarrow 2\,PCl_5(s) \quad \Delta_r H^{(2)} = -887\text{kJ} \end{aligned} \tag{1.16.12}$$

In order to get these two given reactions to add to the one of interest, we first divide both reactions by **2**:

$$\begin{aligned} &(1') \quad P(s) + \tfrac{3}{2}Cl_2(g) \longrightarrow PCl_3(l) \quad \Delta_r H^{(1')} = -320\text{kJ} \\ &(2') \quad P(s) + \tfrac{5}{2}Cl_2(g) \longrightarrow PCl_5(s) \quad \Delta_r H^{(2')} = -442.5\text{kJ} \end{aligned} \tag{1.16.13}$$

Next, write reaction (1′) in reverse:

$$(1'') \quad PCl_3(l) \longrightarrow P(s) + \tfrac{3}{2}Cl_2(g) \quad \Delta_r H^{(1'')} = 320\text{kJ} \tag{1.16.14}$$

Finally, when we add (1″) to (2′), we obtain the original reaction. The overall reaction enthalpy is, therefore,

$$\Delta_r H = \Delta_r H^{(1'')} + \Delta_r H^{(2')} = 320\text{kJ} - 443.5\text{kJ} = -123.4\text{kJ} \tag{1.16.15}$$

Phase Changes

Although phase changes are not chemical reactions, a quantity of heat is still required, for example, to transform ice at $0°C$ to water at $0°C$. This quantity of heat is called the *enthalpy of fusion:*

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H_{\text{fus}} = +6.007\text{kJ} \tag{1.16.16}$$

Similarly, a quantity of heat is necessary to transform water at $100°C$ to steam at $100°C$. This quantity is known as the *enthalpy of vaporization*:

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H_{\text{vap}} = +40.7\text{kJ} \tag{1.16.17}$$

Standard-State Enthalpies

Absolute enthalpies of substances, like absolute energies, cannot be measured -- only changes in enthalpy can be measured. This, it is necessary to have a reference state, just as it is necessary to establish a reference point for computing potential energies. The reference state for reaction enthalpies is called the *standard state* and is defined as follows:

1. For liquids and solids, the standard state is the thermodynamically stable state at a pressure of **1** atm and a specified temperature. The stable state could be liquid or solid.
2. For gases, the standard state is the gaseous state at a pressure of **1** atm and a specified temperature, based on the assumption of ideal gas behavior.
3. For dissolved species, the standard state is a **1** M solution at a pressure of **1** atm and specified temperature, based on the assumption of ideal solution behavior.

Given this definition of the standard state, a scale needs to be defined by arbitrarily setting the enthalpies of selected reference substances to **0**. The choice of reference is the following: *the enthalpies of chemical elements in their standard states at* **298.15** *K are defined to be* **0**. For elements that can exist in several forms, we choose that form which is most stable at **1** atm and **298.15** K. For example, oxygen can exist as $O_2(g)$ or $O_3(g)$. The former is more stable, so it is defined to have a **0** enthalpy. Carbon can exist as graphite, diamond, or fullerene. Graphite is the most stable of these at **1** atm and **298.15** K, sot it is assigned an enthalpy of **0**. For any reaction, the standard state enthalpy is denoted $\Delta H°$.

In order to have useful enthalpy data to tabulate, one more concept is introduced. the *standard enthalpy of formation* of a compound is the enthalpy change for a reaction that produces **1** mol of the compound from its elements at **1** atm pressure and $25°C$. For example, the standard enthalpy of formation of water is the standard enthalpy of the reaction:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta_f H° = -285.83\text{kJ} \tag{1.16.18}$$

For species that dissolve into ions in solution, ions of both positive and negative charge will be produced. Clearly, we cannot measure the enthalpy of formation of ions of only one type of charge, rather, only the sum of the enthalpies can be measured. Thus, one more arbitrary assignment must be made, namely, that the standard enthalpy of formation of $H^+(aq)$ is **0**

An example of the use of tabulated standard state enthalpies, consider the following:

What is the standard state enthalpy of the reaction

$$C(s) + CO_2(g) \longrightarrow 2\,CO \tag{1.16.19}$$

We need to consider this as a two-step process, wherein CO_2 is broken down into its elements, then these elements recombine to form $CO(g)$. The two steps of the reaction are

$$CO_2(g) \longrightarrow C(s) + O_2(g) \tag{1.16.20}$$
$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \tag{1.16.21}$$

It is easy to verify that the sum of these two reactions reproduces the desired reaction above. In Appendix D of the book, the following standard enthalpies of formation are given:

$$\begin{aligned} C(s) + O_2(g) &\longrightarrow CO_2(g) \quad \Delta_f H° = -393.51\text{kJ} \\ C(s) + \tfrac{1}{2}O_2(g) &\longrightarrow CO(g) \quad \Delta_f H° = -110.52\text{kJ} \end{aligned} \tag{1.16.22}$$

Thus, for the reaction we are considering, the standard enthalpy of formation is the sum of the standard enthalpies of formation for the two individual steps:

$$\Delta H° = -\Delta_f H°(CO_2) + 2\Delta_f H°(CO) = 172.47\text{kJ} \tag{1.16.23}$$

As a second example, consider the reaction

$$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \tag{1.16.24}$$

Calculate the reaction enthalpy at the standard state using tabulated formation enthalpies.

The three formation reactions are

$$\begin{aligned} (1) \quad C(s) + O_2(g) &\longrightarrow CO_2(g) \quad \Delta_f H° = -393.5\text{kJ} \\ (2) \quad H_2(g) + \tfrac{1}{2}O_2(g) &\longrightarrow H_2O(l) \quad \Delta_f H° = -285.8\text{kJ} \\ (3) \quad 2\,C(s) + H_2(g) &\longrightarrow C_2H_2(g) \quad \Delta_f H° = 226.7\text{kJ} \end{aligned} \tag{1.16.25}$$

We just need to combine these to give the correct overall reaction. We simply need to multiply the first reaction by **(2)** and write reaction **(3)** in reverse. This gives

$$\begin{aligned} (1') \quad 2\,C(s) + 2\,O_2(g) &\longrightarrow 2\,CO_2(g) \quad \Delta_f H° = -787\text{kJ} \\ (2) \quad H_2(g) + \tfrac{1}{2}O_2(g) &\longrightarrow H_2O(l) \quad \Delta_f H° = -258.8\text{kJ} \\ (3') \quad C_2H_2(g) &\longrightarrow 2\,C(s) + H_2(g) \quad \Delta_f H° = -226.7\text{kJ} \end{aligned} \tag{1.16.26}$$

Summing these gives the correct overall reaction. Thus, the overall reaction enthalpy is

$$\Delta_r H^\circ = -787\text{kJ} - 226.7\text{kJ} - 285.8\text{kJ} = -1299.5\text{kJ/mol} \tag{1.16.27}$$

As one final consideration of standard state enthalpies, we define the *bond enthalpy* as the enthalpy required to break 1 mol of a particular chemical bond in the gas phase. Since energy is required to break a chemical bond, bond enthalpies are always positive. An example of a bond enthalpy is the breaking of $C-H$ bond in methane:

$$CH_4(g) \longrightarrow CH_3(g) + H(g) \qquad \Delta H^o = 438\text{kJ} \tag{1.16.28}$$

Although the products in this reaction are not stable, i.e., they react quickly with other molecules, it is possible to produce such reactions in the lab, and study properties of the products over the period of their brief existence. This, then, is how bond enthalpies are tabulated. Often, bond enthalpies are tabulated as averages of a particular bond breaking, e.g. a $C-H$ bond, over many compounds. Given the relative constancy of bond enthalpies of a particular kind of bond over different molecules, such an average is a good measure of the bond enthalpy one might expect in an arbitrary specific situation.

Temperature Dependence of Reaction Enthalpies

Recall that the constant-pressure heat capacity C_P is given by

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.16.29}$$

For an ideal gas, C_P is independent of temperature, however, for non-ideal systems, C_P does depend on T:

$$C_P(T) = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.16.30}$$

If we wish to consider the reaction enthalpy at a temperature other than that of the standard state, where enthalpies are tabulated, we can use Equation 17.29 to obtain the enthalpy at the desired temperature. Integrating both sides of Equation 17.29 from a temperature T_1 to T_2, we obtain

$$\int_{T_1}^{T_2} C_P(T)\,dT = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_P dT \tag{1.16.31}$$

$$\int_{T_1}^{T_2} C_P(T)\,dT = H(T_2) - H(T_1) \tag{1.16.32}$$

The use of Equation 17.30, of course, assumes that the $H(T)$ is everywhere smooth and differentiable, so that it can be integrated. However, if we plot the molar enthalpy difference $\bar{H}(T) - \bar{H}(0)$ for a real substance such as benzene, we find a curve like that shown in the figure below.

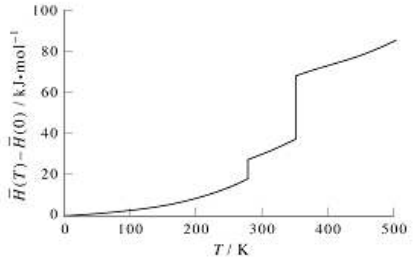


FIG 17.1: *Plot of molar enthalpy $\bar{H}(T) - \bar{H}(0)$ for benzene. Discontinuities in the plot occur at points of phase transitions from solid to liquid T_{melt} and from liquid to gas T_{vap}.*

There are two temperatures at which $H(T)$ exhibits a discontinuity. These two temperatures are the melting temperature T_{melt} of the solid and the vaporization temperature T_{vap} of the liquid. According to our discussion of phase changes, the heat needed to effect these two phase changesa re $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$, respectively. At these temperatures, $C_P = \partial H/\partial T$ diverges, and we cannot smoothly integrate through these divergences. In fact, divergence of the heat capacity is one of the signatures of a phase transition. As long as $T < T_{\text{melt}}$ we can smoothly integrate C_P to obtain a value for $H(T)$:

$$H(T) - H(0) = \int_0^T C_P(T')\,dT' \tag{1.16.33}$$

However, if we are interested in a temperature $T > T_{\text{melt}}$, then we must treat the discontinuity as a special point. Fortunately, we already know the enthalpy change at this point, i.e., $\Delta_{\text{fus}}H$, and we can simply add it in. Thus, for $T > T_{\text{melt}}$. we would calculate $H(T)$ as follows:

$$H(T) - H(0) = \int_0^{T_{\text{melt}}} C_P(T')\,dT' + \Delta_{\text{fus}}H + \int_{T_{\text{melt}}}^{T} C_P(T')\,dT' \tag{1.16.34}$$

The same holds for $T > T_{\text{vap}}$. When we reach the discontinuity at T_{vap}, we simply add in the enthalpy of vaporization $\Delta_{\text{vap}}H$:

$$\begin{aligned} &H(T) - H(0) \\ &= \int_0^{T_{\text{melt}}} C_P(T')\,dT' + \Delta_{\text{fus}}H + \int_{T_{\text{melt}}}^{T_{\text{vap}}} C_P(T')\,dT' + \Delta_{\text{vap}}H + \int_{T_{\text{vap}}}^{T} C_P(T')\,dT' \end{aligned} \tag{1.16.35}$$

Example 17.3

Consider the reaction

$$CO_{(g)} + H_2O_{(g)} \longrightarrow H_{2(g)} + CO_{2(g)} \tag{1.16.36}$$

For this reaction, the heat capacity has the following temperature dependence

$$C_P(T) = a + bT + cT^2 \tag{1.16.37}$$

where a, b, and c are constants. Calculate the reaction enthalpy at $800\ K$ for this reaction given the following data:

- For CO: $a = 26.86$, $b = 6.99 \times 10^{-3}$, $c = 8.20 \times 10^{-7}$
- For H_2O: $a = 30.98$, $b = 9.62 \times 10^{-3}$, $c = 11.84 \times 10^{-7}\backslash$
- For CO_2: $a = 25.98$, $b = 43.51 \times 10^{-3}$, $c = -184.32 \times 10^{-7}$
- For H_2: $a = 26.08$, $b = -0.84 \times 10^{-3}$, $c = 201.3 \times 10^{-7}$

The units of a, b, and c are J $\cdot$ mol$^{-1}\cdot$ K^{-1}, J $\cdot$ mol$^{-1}\cdot$ K^{-2}, and J $\cdot$ mol$^{-1}\cdot$ K^{-3}, respectively. Standard-state formation enthalpies for CO, H_2O, CO_2, and H_2 are -110.52 kJ/mol, -241.82 kJ/mol, -393.51 kJ/mol, and 0 kJ/mol, respectively.

Solution

Since this is already a gas-phase reaction, we do not need to worry about melting or vaporization, so we can smoothly integrate $C_P(T)$ from the standard state, where $T = 298$ K to the desired $800\ K$. Since our reference state is $298\ K$, the integral we need is

$$\Delta_f H(800) = \Delta_f H^\circ + \int_{T_0}^{T_f} C_P(T)\,dT \tag{1.16.38}$$

where $T_0 = 298\ K$ and $T_f = 800\ K$. The integral is

$$\int_{T_0}^{T_f} C_P(T)\,dT = a(T_f - T_0) + \frac{1}{2}b\left(T_f^2 - T_0^2\right) + \frac{1}{3}c\left(T_f^3 - T_0^3\right) \tag{1.16.39}$$

Plugging in the data, we obtain

$$\Delta_f H^{(800)}(CO) = -94.981\text{kJ/mol} \tag{1.16.40}$$
$$\Delta_f H^{(800)}(CO_2) = -370.883\text{kJ/mol} \tag{1.16.41}$$
$$\Delta_f H^{(800)}(H_2O) = -223.731\text{kJ/mol} \tag{1.16.42}$$
$$\Delta_f H^{(800)}(H_2) = 14.668\text{kJ/mol} \tag{1.16.43}$$

Therefore, the overall reaction enthalpy is

$$\Delta_r H^{(800)} = \Delta_f H^{(800)}(H_2) + \Delta_f H^{(800)}(CO_2) - \Delta_f H^{(800)}(H_2O) - \Delta_f H^{(800)}(CO) \tag{1.16.44}$$
$$= 14.668 - 370.883 + 94.981 + 223.731 = -37.503\text{kJ/mol} \tag{1.16.45}$$

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1.17: Chemical Equilibria

General Thermodynamic Treatment of Chemical Equilibrium

Consider an equilibrium reaction

$$a\mathrm{A} + b\mathrm{B} \leftrightharpoons c\mathrm{C} + d\mathrm{D} \tag{1.17.1}$$

We do not specify any phases, as we will treat the reaction generally using activities. An equilibrium reaction is one that can proceed in both directions, as indicated by the $\leftrightharpoons$ symbol replacing the usual $\longrightarrow$ in the chemical equation.

Recall that the molar free energy $\Delta\tilde{G}_j$ for compound j in the reaction in terms of its activity a_j as

$$\Delta\tilde{G} = \Delta\tilde{G}^{\circ} + RT\ln a_j \tag{1.17.2}$$

where $\Delta\tilde{G}^{\circ}$ is the molar Gibbs free energy at a reference state, taken to be the standard state. Now the change in the Gibbs free energy of the reaction is

$$\begin{aligned}
\Delta_r G &= c\Delta\tilde{G}_{\mathrm{C}} + d\Delta\tilde{G}_{\mathrm{D}} - a\Delta\tilde{G}_{\mathrm{A}} - b\Delta\tilde{G}_{\mathrm{B}} && (1.17.3)\\
&= c\Delta\tilde{G}^{\circ}_{\mathrm{C}} + d\Delta\tilde{G}^{\circ}_{\mathrm{D}} - a\Delta\tilde{G}^{\circ}_{\mathrm{A}} - b\Delta\tilde{G}^{\circ}_{\mathrm{B}} && (1.17.4)\\
&+ RT\left[c\ln a_{\mathrm{C}} + d\ln a_{\mathrm{D}} - a\ln a_{\mathrm{A}} - b\ln a_{\mathrm{B}}\right] && (1.17.5)\\
&= \Delta_r G^{\circ} + RT\left[\ln a_{\mathrm{C}}^{c} + \ln a_{\mathrm{D}}^{d} - \ln a_{\mathrm{A}}^{a} - \ln a_{\mathrm{B}}^{b}\right] && (1.17.6)\\
&= \Delta_r G^{\circ} + RT\ln\left[\frac{a_{\mathrm{C}}^{c}a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a}a_{\mathrm{B}}^{b}}\right] && (1.17.7)
\end{aligned}$$

At equilibrium, we need $\Delta_r G = 0$. This gives the condition for chemical equilibrium

$$-\Delta_r G^{\circ} = RT\ln\left[\frac{a_{\mathrm{C}}^{c}a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a}a_{\mathrm{B}}^{b}}\right] \tag{1.17.8}$$

We define the equilibrium constant K as

$$K = \frac{a_{\mathrm{C}}^{c}a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a}a_{\mathrm{B}}^{b}} \tag{1.17.9}$$

which implies that

$$\begin{aligned}
-\Delta_r G^{\circ} &= RT\ln K\\
K &= e^{-\Delta_r G^{\circ}/RT}
\end{aligned} \tag{1.17.10}$$

Equilibrium of Gas-Phase Chemical Reactions: Ideal Gases

Consider a generic gas-phase reaction

$$a\mathrm{A}(g) + b\mathrm{B}(g) \leftrightharpoons c\mathrm{C}(g) + d\mathrm{D}(g) \tag{1.17.11}$$

If we treat the gases as ideal gases, then recall that

$$a_j = \frac{P_j}{P_j^{\circ}} \tag{1.17.12}$$

and the change in the molar Gibbs free energy when the pressure of an ideal gas changes from the standard value P° to some other pressure P at temperature T is

$$\Delta\tilde{G}^{\circ} + RT\ln\left(\frac{P}{P^{\circ}}\right) \tag{1.17.13}$$

Let P_{A}, P_{B}, P_{C}, and P_{D} be the partial pressures of each of the four species in the equilibrium state. The free energy of each species in the gas is defined as a free energy *change* with respect to its *standard state*. For gases, we had defined this to be a partial

pressure of $1\ \text{atm}$. Thus, let us the standard state partial pressure $P^\circ = 1\ \text{atm}$. Then, in the above reaction, a moles of A react, so the free energy of A is

$$a\Delta G(\text{A}) = aRT \ln\left(\frac{P_\text{A}}{P^\circ}\right) + a\Delta_\text{f}G^\circ(\text{A}) \tag{1.17.14}$$

Similarly, for B, C, and D, we have

$$b\Delta G(\text{B}) = bRT \ln\left(\frac{P_\text{B}}{P^\circ}\right) + b\Delta_\text{f}G^\circ(\text{B}) \tag{1.17.15}$$

$$c\Delta G(\text{C}) = cRT \ln\left(\frac{P_\text{C}}{P^\circ}\right) + c\Delta_\text{f}G^\circ(\text{C}) \tag{1.17.16}$$

$$d\Delta G(\text{D}) = dRT \ln\left(\frac{P_\text{D}}{P^\circ}\right) + d\Delta_\text{f}G^\circ(\text{D}) \tag{1.17.17}$$

where $\Delta_\text{f}G^\circ(X)(X = \text{A}, \text{B}, \text{C}, \text{D})$ is the standard energy of formation of X. Thus, the overall free energy change of for the reaction is

$$\Delta_\text{r}G = d\Delta G(\text{D}) + c\Delta G(\text{C}) - a\Delta G(\text{A}) - b\Delta G(\text{B}) \tag{1.17.18}$$

$$= d\Delta_\text{f}G^\circ(\text{D}) + c\Delta_\text{f}G^\circ(\text{C}) - a\Delta_\text{f}G^\circ(\text{A}) - b\Delta_\text{f}G^\circ(\text{B}) \tag{1.17.19}$$

$$+ dRT \ln\left(\frac{P_\text{D}}{P^\circ}\right) + cRT \ln\left(\frac{P_\text{C}}{P^\circ}\right) - aRT \ln\left(\frac{P_\text{A}}{P^\circ}\right) - bRT \ln\left(\frac{P_\text{B}}{P^\circ}\right) \tag{1.17.20}$$

The first line is just the standard free energy change $\Delta_\text{r}G^\circ$ for the reaction. The second line can be simplified giving

$$\Delta_\text{r}G = \Delta_\text{r}G^\circ + RT\left[d \ln\left(\frac{P_\text{D}}{P^\circ}\right) + c \ln\left(\frac{P_\text{C}}{P^\circ}\right) - a \ln\left(\frac{P_\text{A}}{P^\circ}\right) - b \ln\left(\frac{P_\text{B}}{P^\circ}\right)\right] \tag{1.17.21}$$

$$= \Delta_\text{r}G^\circ + RT\left[\ln\left(\frac{P_\text{D}}{P^\circ}\right)^d + \ln\left(\frac{P_\text{C}}{P^\circ}\right)^c - \ln\left(\frac{P_\text{A}}{P^\circ}\right)^a - \ln\left(\frac{P_\text{B}}{P^\circ}\right)^b\right] \tag{1.17.22}$$

$$= \Delta_\text{r}G^\circ + RT \ln\left[\frac{(P_\text{D}/P^\circ)^d(P_\text{C}/P^\circ)^c}{(P_\text{A}/P^\circ)^a(P_\text{B}/P^\circ)^b}\right] \tag{1.17.23}$$

Since the Gibbs free energy change $\Delta G = 0$ at equilibrium, we are left with

$$\Delta_\text{r}G^\circ = -RT \ln\left[\frac{(P_\text{D}/P^\circ)^d(P_\text{C}/P^\circ)^c}{(P_\text{A}/P^\circ)^a(P_\text{B}/P^\circ)^b}\right] \tag{1.17.24}$$

The quantity in brackets is called the equilibrium constant, K for the reaction:

$$K = \frac{(P_\text{D}/P^\circ)^d(P_\text{C}/P^\circ)^c}{(P_\text{A}/P^\circ)^a(P_\text{B}/P^\circ)^b} \tag{1.17.25}$$

and is, itself, a thermodynamic quantity related to the standard Gibbs free energy change by

$$K = e^{-\Delta_\text{r}G^\circ/RT} \tag{1.17.26}$$

We can see that K is a direct measure of whether reactants, products or neither in particular is favored in an equilibrium state. If K is large ($K \gg 1$), $\Delta_\text{r}G^\circ < 0$, and the reaction favors products and if K is very small ($K \ll 1$), $\Delta_\text{r}G^\circ > 0$, and reactants are favored. For K near 1, there is likely to be roughly equal amounts of reactant and product in the equilibrium state.

Note, also, that K can be a sensitive function of temperature, a point we will return to later. Also, due to the presence of P° in the equation, K is a dimensionless quantity. Finally, since the reference partial pressure is $P^\circ = 1\ \text{atm}$, if we insist that all partial pressures be expressed in atm, then we do not need to include the P° explicitly in Equation 1.17.24 for K and can simply write:

$$K = \frac{P_\text{C}^c P_\text{D}^d}{P_\text{A}^a P_\text{B}^b} \tag{1.17.27}$$

One use of equilibrium constants is the calculation of equilibrium compositions of reactions from given starting conditions. The following example illustrates this:

Quantity	$H_2(g)$	$I_2(g)$	$HI(g)$
Initial partial pressure (atm)	1.9890	1.710	0.0
Change in partial pressure (atm)	$-x$	$-x$	$+2x$
Equilibrium partial pressure (atm)	$1.9890 - x$	$1.710 - x$	$+2x$

(1.17.28)

Example 1.17.1

H_2 gas and I_2 gas react quickly at $600\ \text{K}$ to form HI gas according to an equilibrium reaction:

$$H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$$

The equilibrium constant for the reaction is known to be 92.6. If the initial partial pressures of H_2 and I_2 are $1.980\ \text{atm}$ and $1.710\ \text{atm}$, respectively, what are the equilibrium partial pressures of each gas?

Solution

The expression for the equilibrium constant is

$$K = \frac{(P_{HI})^2}{P_{H_2} P_{I_2}}$$

Let x be the change in partial pressure of one of the gases, say H_2 gas. We begin by setting up the table described earlier.

The stoichiometry requires the factor of 2 in front for the change in partial pressure of HI. Substitution into the expression for the equilibrium constant gives

$$92.6 = \frac{(2x)^2}{(1.980 - x)(1.710 - x)}$$

This expression leads to a quadratic equation for x:

$$88.6x^2 - 341.694x + 313.525 = 0$$

Applying the quadratic formula gives

$$x = \frac{341.694 \pm \sqrt{(341.694)^2 - 4(88.6)(313.525)}}{2(88.6)}$$

The two solutions are

$$x = 1.5044\ \text{atm} \qquad x = 2.3522\ \text{atm}$$

The larger of these would lead to negative equilibrium partial pressures, which is an unphysical situation. Thus, we discard this solution and keep the smaller of the two. Then the equilibrium partial pressures are

$$\begin{aligned} P_{HI} &= 2 \times 1.5044\ \text{atm} = 3.0088\ \text{atm} \\ P_{H_2} &= 1.980\ \text{atm} - 1.5044\ \text{atm} = 0.4756\ \text{atm} \\ P_{I_2} &= 1.710\ \text{atm} - 1.5044\ \text{atm} = 0.2056\ \text{atm} \end{aligned}$$

It is always a good idea to check the numbers by substituting back into the equilibrium expression:

$$\frac{(3.0088)^2}{(0.4756)(0.2056)} = 92.6$$

so the answers are correct.

Gas-phase reactions away from equilibrium

If the reactants and products are perturbed from their equilibrium state, then the associated change in the Gibbs free energy is given by the full expression we derived previously:

$$\Delta_r G = \Delta_r G^\circ + RT \ln \left[\frac{(P_D/P^\circ)^d (P_C/P^\circ)^c}{(P_A/P^\circ)^a (P_B/P^\circ)^b} \right] \tag{1.17.29}$$

In this case, although the term in brackets looks like an equilibrium constant, it is *not* one. One can only designate this expression as K if $\Delta_r G = 0$. The general definition of this term in brackets, is designated as q,

$$q = \frac{(P_D/P^\circ)^d (P_C/P^\circ)^c}{(P_A/P^\circ)^a (P_B/P^\circ)^b} \tag{1.17.30}$$

which is called the *reaction quotient*. Only in equilibrium does it follow that $q = K$. However, since $\Delta_r G^o = -RT \ln K$, it follows that

$$\Delta_r G = -RT \ln K + RT \ln q = RT \ln \left(\frac{q}{K} \right) \tag{1.17.31}$$

If the reaction is perturbed from its equilibrium state, then the sign of $\Delta_r G$ tell us which way the reaction will proceed in order to restore equilibrium according to Le Chatelier's principle. However, the sign of $\Delta_r G$ translates directly a condition on the ratio q/K. If $\Delta_r G < 0$, then the reaction proceeds spontaneously from left to right as written and $q < K$. If $\Delta_r G > 0$, the reaction proceeds spontaneously in the reverse direction (right to left), and $q > K$. At equilibrium, $q = K$, so if the system is perturbed, the reaction will proceed in a direction that restores the condition $q = K$. The following example illustrates this:

Example 1.17.2

Consider the reaction:

$$H_2(g) + I_2(g) \leftrightharpoons 2HI(g) \tag{1.17.32}$$

and suppose that it is in equilibrium with partial pressures:

$$P_{H_2} = 0.4756 \text{ atm} \qquad P_{I_2} = 0.2056 \text{ atm} \qquad P_{HI} = 3.009 \text{ atm} \tag{1.17.33}$$

Enough H_2 is added to increase its partial pressure to 2.00 atm. When equilibrium is restored, what will be the partial pressures of each three gases?

Solution

First calculate the equilibrium constant from the equilibrium partial pressures:

$$K = \frac{IP_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(3.009)^2}{(0.4756)(0.2056)} = 92.6 \tag{1.17.34}$$

When the pressure of H_2 is increased, what happens to the reaction quotient?

$$q = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(3.009)^2}{(2.00)(0.2056)} = 22.02 \tag{1.17.35}$$

So, $q < K$. Now set up the table to figure out by how much each partial pressure will change when equilibrium is restored.

Quantity	$H_2(g)$	$I_2(g)$	$HI(g)$
Initial partial pressure (atm)	2.0000	0.2056	3.0090
Change in partial pressure (atm)	$-x$	$-x$	$+2x$
Equilibrium partial pressure (atm)	$2.0000 - x$	$0.2056 - x$	$3.0090 + 2x$

(1.17.36)

Here "initial" stands for the partial pressures just after the pressure of H_2 is increased.

Substitution into the equilibrium constant expression gives:

$$\frac{(3.0090 + 2x)^2}{(2.0000 - x)(0.2056 - x)} = 92.6 \tag{1.17.37}$$

which leads to the quadratic equation:

$$88.6x^2 - 216.275x + 29.023 = 0 \tag{1.17.38}$$

whose roots are

$$x = 0.1425 \text{ atm} \qquad x = 2.299 \text{ atm} \tag{1.17.39}$$

The second of these would lead to negative partial pressures, so we discard it. Using the first root, we obtain the new equilibrium partial pressures:

$$\begin{aligned} P_{H_2} &= 2.0000 - 0.1425 = 1.86 \text{ atm} \\ P_{I_2} &= 0.2056 - 0.1425 = 0.0631 \text{ atm} \\ P_{HI} &= 3.009 + 2(0.1425) = 3.29 \text{ atm} \end{aligned} \tag{1.17.40}$$

which shows that the new partial pressures are not the same as the old when equilibrium is restored in the system.

When treating the gases as ideal gases, we can use the ideal gas law to re-express the equilibrium constant in terms of densities rather than pressures. Since $P = nRT/V = \rho RT$, the partial pressure of each gas if $P_A = \rho_A RT$, etc. Substituting this into the equilibrium constant expression, we find

$$K = \frac{\rho_C^c \rho_D^d}{\rho_A^a \rho_B^b} \left(\frac{RT}{P^\circ}\right)^{c+d-a-b} \equiv K_c \left(\frac{RT}{P^\circ}\right)^{c+d-a-b} \tag{1.17.41}$$

where K_c is the density-dependent part of the equilibrium constant. We can see from this expression that K is a rather sensitive function of temperature given its exponential dependence on the difference of stoichiometric coefficients.

Another way to see the sensitive temperature dependence is to recall that

$$K = e^{-\Delta_r G^\circ / RT} \tag{1.17.42}$$

However, since $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, this becomes

$$K = e^{-\Delta_r H^\circ / RT} e^{-\Delta_r S^\circ / R} \tag{1.17.43}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$ and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta_r H^\circ}{R}\frac{1}{T} + \frac{\Delta_r S^\circ}{R} \tag{1.17.44}$$

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 $-dhs/R$ and intercept $\Delta_r S^\circ/R$. 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 $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are only very weakly dependent on T, which is usually valid.

Treatment of Equilibrium for Real Gases

In many instances, the ideal-gas approximation is insufficient in treating gas-phase reactions. In such cases, we need to be able to correct for this approximation. Recall that we can do this using the virial equation of state when the density of the gas is not too high.

The form of the virial equation of state is

$$\frac{PV}{nRT} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots \tag{1.17.45}$$

where $B_2(T), B_3(T), \ldots$ are the virial coefficients. Since $V/n = \bar{V}$, this is also

$$\frac{P\bar{V}}{RT} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots \tag{1.17.46}$$

More importantly, if we assume that the virial coefficients properly correct for non-ideal behavior and approximate, at each order $\rho \approx P/RT$, then we see that the virial equation of state can be written as a polynomial in P rather than in ρ:

$$\frac{P\bar{V}}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + \cdots \tag{1.17.47}$$

where $B_{2P}(T), B_{3P}(T), \ldots$ are the virial coefficients for the pressure expansion. As written, the modified virial coefficients are

$$B_{2P}(T) = \frac{B_2(T)}{RT}, \quad B_{3P}(T) = \frac{B_3(T)}{(RT)^2}, \ldots \tag{1.17.48}$$

However, we can improve upon this approximation as follows: First use the standard virial equation to write

$$P = \rho RT\left[1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots\right] \tag{1.17.49}$$

and use this to re-express the pressure virial equation as

$$\frac{P\bar{V}}{RT} = 1 + B_{2P}(T)\left(\rho RT\left[1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots\right]\right) \tag{1.17.50}$$

$$+ B_{3P}(T)\left(\rho RT\left[1+B_2(T)\rho+B_3(T)\rho^2+\cdots\right]\right)^2 + \cdots \tag{1.17.51}$$

The two virial equations must be equal so we set

$$1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots = 1 + B_{2P}(T)\left(\rho RT\left[1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots\right]\right) \tag{1.17.52}$$

$$+ B_{3P}(T)\left(\rho RT\left[1+B_2(T)\rho+B_3(T)\rho^2+\cdots\right]\right)^2 + \cdots \tag{1.17.53}$$

and we equate like powers of ρ. Thus, the terms linear in ρ on both sides gives us

$$B_2(T)\rho = (\rho RT)\, B_{2P}(T) \tag{1.17.54}$$

or

$$B_{2P}(T) = \frac{B_2(T)}{RT} \tag{1.17.55}$$

The terms quadratic in ρ on both sides give

$$B_{2P}(T)B_2(T)\rho^2 RT + B_{3P}(T)(\rho RT)^2 = B_3(T)\rho^2 \tag{1.17.56}$$

Solving for $B_{3P}(T)$ and using the fact that $B_{2P}(T) = B_2(T)/RT$, we obtain

$$B_{3P}(T) = \frac{B_3(T) - (B_2(T))^2}{(RT)^2} \tag{1.17.57}$$

and so forth.

In order to use the virial equation of state to calculate the Gibbs free energy, we use the fact that

$$\left(\frac{\partial G}{\partial P}\right)_{N,T} = V \tag{1.17.58}$$

where V is the average volume. Similarly, the average molar volume is

$$\left(\frac{\partial \tilde{G}}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} \tag{1.17.59}$$

Integrating this respect to pressure from the standard state P^o to an arbitrary P gives

$$\Delta\tilde{G} = \int_{P^o}^{P}\left(\frac{\partial \tilde{G}}{\partial P'}\right) dP' = \int_{P^o}^{P} \bar{V}\, dP' \tag{1.17.60}$$

From the virial equation of state

$$\bar{V} = \frac{RT}{P}\left[1 + B_{2P}(T)P + B_{3P}(T)P^2 + \cdots\right] \tag{1.17.61}$$

Hence,

$$\Delta\tilde{G} = RT\int_{P^o}^{P}\left[\frac{1}{P'} + B_{2P}(T) + B_{3P}(T)P' + \cdots\right] dP' + \Delta\tilde{G}^o \tag{1.17.62}$$

$$= RT\ln\left(\frac{P}{P^o}\right) B_{2P}(T)(P - P^o) + \frac{1}{2}B_{3P}(T)(P^2 - (P^o)^2) + \cdots + \Delta\tilde{G}^o \tag{1.17.63}$$

$$\equiv \Delta\tilde{G}^o + RT\ln\left(\frac{f(P,T)}{f^o}\right) \tag{1.17.64}$$

where

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$$\ln\left(\frac{f(P,T)}{f^\circ}\right) = \ln\left(\frac{P}{P^\circ}\right) + B_{2P}(T)(P-P^\circ) + \frac{1}{2}B_{3P}(T)(P^2-(P^\circ)^2) + \cdots \tag{1.17.65}$$

$$\frac{f(P,T)}{f^\circ} = \frac{P}{P^\circ} e^{B_{2P}(T)(P-P^\circ)+B_{3P}(T)(P^2-(P^\circ)^2)/2+\cdots} \tag{1.17.66}$$

where $f(P,T)$ is called the *fugacity* of the gas. Equation 18.36 also defines the gas-phase activity coefficient

$$\frac{f(P,T)}{f^\circ} = \frac{\gamma P}{P^\circ} \tag{1.17.67}$$

Applying the same analysis to $\Delta\tilde{G}$ to the gas-phase reaction

$$a\mathrm{A}(g) + b\mathrm{B}(g) \leftrightharpoons c\mathrm{C}(g) + d\mathrm{D}(g) \tag{1.17.68}$$

as was done for the ideal gas, we obtain an expression for $\Delta_r G$ in terms of fugacities of each gas:

$$\Delta_r G = \Delta_r G^\circ + RT\ln\left[\frac{(f_\mathrm{D}(P_\mathrm{D},T)/f^\circ)^d (f_\mathrm{C}(P_\mathrm{C},T)/f^\circ)^c}{(f_\mathrm{A}(P_\mathrm{A},T)/f^\circ)^a (f_\mathrm{B}(P_\mathrm{B},T)/f^\circ)^b}\right] \tag{1.17.69}$$

and setting $\Delta_r G = 0$, the standard Gibbs free energy takes the usual form $\Delta_r G^\circ = -RT\ln K$, where

$$K = \frac{(f_\mathrm{D}(P_\mathrm{D},T)/f^\circ)^d (f_\mathrm{C}(P_\mathrm{C},T)/f^\circ)^c}{(f_\mathrm{A}(P_\mathrm{A},T)/f^\circ)^a (f_\mathrm{B}(P_\mathrm{B},T)/f^\circ)^b} \tag{1.17.70}$$

In order to see how non-ideality complicates equilibrium calculations, consider the first example above involving the reaction

$$H_2(g) + I_2(g) \leftrightharpoons 2HI(g) \tag{1.17.71}$$

The equilibrium constant for the reaction is 92.6. If the initial partial pressures of H_2 and I_2 are $1.980\ \mathrm{atm}$ and $1.710\ \mathrm{atm}$, then we can use $P_{HI} = 2x$, $P_{H_2} = 1.98 - x$, $P_{I_2} = 1.71 - x$, and taking $P^\circ = 1\ \mathrm{atm}$, if we just worked to lowest order in the virial equation (involving only the $B_2(T)$ term), the equation we would need to solve for x would be

$$K = 92.6 = \frac{\left(2xe^{B_{2P}^{(HI)}(T)(2x-1)}\right)^2}{\left((1.98-x)\,e^{B_{2P}^{(H_2)}(T)(0.98-x)}\right)\left((1.71-x)\,e^{B_{2P}^{(I_2)}(T)(0.71-x)}\right)} \tag{1.17.72}$$

which is simply too complicated to be solved algebraically. In the next lecture, we will outline a procedure that can be used to solve such equations iteratively, assuming that the non-ideal nature of the equilibrium is not too large. Otherwise, the equation would need to be solved by numerical procedures.

Equilibrium of Solution-Phase Chemical Reactions: Ideal Solutions

Consider the generic aqueous reaction (what we say for aqueous reaction is equally applicable in any solvent):

$$a\mathrm{A}(aq) + b\mathrm{B}(aq) \leftrightharpoons c\mathrm{C}(aq) + d\mathrm{D}(aq) \tag{1.17.73}$$

Recall that the molar Gibbs free energy for species j in a solution is

$$\Delta\tilde{G}_j^{\,(\mathrm{soln})} = \mu_j^{(\mathrm{soln})} + \mu_j^*(\mathrm{liquid}) + RT\ln x_j \tag{1.17.74}$$

where x_j is the mole fraction of species j in solution.

Moreover, recall that we derived the following relation between mole fractions and molalities:

$$x_j = \frac{M_1 m_j/1000}{1 + M_1 m/1000} \tag{1.17.75}$$

where M_1 is the molar mass of the solvent, m_j is the molality of species j, and $m = \sum_j m_j$ is the total molality of the solution. If the solution is dilute, then

$$\frac{M_1 m}{1000} \ll 1 \tag{1.17.76}$$

and we can approximate

$$x_j \approx \frac{M_1 m_j}{1000} \tag{1.17.77}$$

For water, $\rho_1 = 1.0\ \mathrm{kg/L}$. But the concentration of solute j is in $(\textbf{moles of solute})/(\textbf{liters of solution})$. The denominator can be approximated with liters of solvent if the solution is dilute, in which case

$$c_j = m_j \rho_1 \tag{1.17.78}$$

so that $m_j = c_j/\rho_1$, and

$$x_j = \frac{M_1 c_j}{1000 \rho_1} = \frac{c_j}{c^*} \tag{1.17.79}$$

where c^* is a reference concentration of the pure solvent. Therefore,

$$\Delta \tilde{G}_j^{\,(\mathrm{soln})} = \mu_j^{(\mathrm{soln})} = \mu_j^*(\mathrm{liquid}) + RT \ln\left(\frac{c_j}{c^*}\right) \tag{1.17.80}$$

Relative to any reference, we can also write

$$\Delta \tilde{G}_j^{\,(\mathrm{soln})} = \mu_j^{(\mathrm{soln})} = \mu_j^{\circ} + RT \ln\left(\frac{c_j}{c^{\circ}}\right) \tag{1.17.81}$$

Denoting the concentrations of species A, B, C, and D in the solution as $[\mathrm{A}]$, $[\mathrm{B}]$, $[\mathrm{C}]$ and $[\mathrm{D}]$, respectively, we can write the molar Gibbs free energies for each species as

$$\Delta \tilde{G}(\mathrm{A}) = RT \ln\left(\frac{[\mathrm{A}]}{c^{\circ}}\right) + \Delta_f G^{\circ}(\mathrm{A}) \tag{1.17.82}$$

$$\Delta \tilde{G}(\mathrm{B}) = RT \ln\left(\frac{[\mathrm{B}]}{c^{\circ}}\right) + \Delta_f G^{\circ}(\mathrm{B}) \tag{1.17.83}$$

$$\Delta \tilde{G}(\mathrm{C}) = RT \ln\left(\frac{[\mathrm{C}]}{c^{\circ}}\right) + \Delta_f G^{\circ}(\mathrm{C}) \tag{1.17.84}$$

$$\Delta \tilde{G}(\mathrm{D}) = RT \ln\left(\frac{[\mathrm{D}]}{c^{\circ}}\right) + \Delta_f G^{\circ}(\mathrm{D}) \tag{1.17.85}$$

Analyzing the overall free energy change

$$\Delta_r G = d\Delta G(\mathrm{D}) + c\Delta G(\mathrm{C}) - a\Delta G(\mathrm{A}) - b\Delta G(\mathrm{B}) \tag{1.17.86}$$

as was done for the gas phase, we find the analogous expression

$$\Delta_r G = \Delta_r G^{\circ} + RT \ln\left[\frac{([\mathrm{D}]/c^{\circ})^d ([\mathrm{C}]/c^{\circ})^c}{([\mathrm{A}]/c^{\circ})^a ([\mathrm{B}]/c^{\circ})^b}\right] \tag{1.17.87}$$

When $\Delta_r G = 0$ at equilibrium, this becomes

$$\Delta_r G^{\circ} = -RT \ln K \tag{1.17.88}$$

where the equilibrium constant is

$$K = \frac{([\mathrm{D}]/c^{\circ})^d ([\mathrm{C}]/c^{\circ})^c}{([\mathrm{A}]/c^{\circ})^a ([\mathrm{B}]/c^{\circ})^b} \tag{1.17.89}$$

and choosing $c^{\circ} = 1\ \mathrm{M}$, we obtain the familiar expression

$$K = \frac{[\mathrm{C}]^c [\mathrm{D}]^d}{[\mathrm{A}]^a [\mathrm{B}]^b} \tag{1.17.90}$$

For non-ideal solutions, the ratio c_j/c° is modified via multiplication by the activity coefficient γ, so that

$$\Delta \tilde{G}_j = \Delta \tilde{G}_j^{\circ} + RT \ln\left(\frac{\gamma c_j}{c^{\circ}}\right) \tag{1.17.91}$$

The importance of activities will be made clear in the next section.

Heterogeneous Equilibria

Heterogeneous equilibria involve more than one phase (solid, liquid, gas, solution,...). Examples of heterogeneous equilibria are phase equilibria, e.g.,

$$H_2O(l) \leftrightharpoons H_2O(g) \tag{1.17.92}$$

Dissolution of solids in solvent, e.g.,

$$I_2(s) \leftrightharpoons I_2(aq) \tag{1.17.93}$$

or

$$CaF_2(s) \leftrightharpoons Ca^{2+}(aq) + 2F^-(aq) \tag{1.17.94}$$

or a solid-solid phase transition, e.g.

$$C(s, \mathrm{gr}) \leftrightharpoons C(s, \mathrm{d}) \tag{1.17.95}$$

Activities enter into the molar Gibbs free energy as

$$\Delta\tilde{G} = \Delta\tilde{G}^\circ + RT \ln a \tag{1.17.96}$$

where a is the activity. In the generic reaction

$$a\mathrm{A}(\varphi_\mathrm{A}) + b\mathrm{B}(\varphi_\mathrm{B}) \leftrightharpoons c\mathrm{C}(\varphi_\mathrm{C}) + d\mathrm{D}(\varphi_\mathrm{D}) \tag{1.17.97}$$

where φ_A, φ_B, φ_C, and φ_D are the phases of $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$, and $\mathbf{D}$, respectively. The equilibrium constant is then given by

$$K = \frac{a_\mathrm{C}^c a_\mathrm{D}^d}{a_\mathrm{A}^a a_\mathrm{B}^b} \tag{1.17.98}$$

The general rule for activities is that activities of pure solids (in their thermodynamically most stable state) and pure liquids are 1, and activities of real gases are

$$a = \frac{f(P,T)}{f^\circ} \tag{1.17.99}$$

As an example, consider the heterogeneous equilibrium

$$C(s) + H_2O(g) \leftrightharpoons CO(g) + H_2(g) \tag{1.17.100}$$

where $C(s)$ is a solid phase other than graphite. The equilibrium constant for this reaction would be

$$K = \frac{(f_{CO(g)}/f^\circ)(f_{H_2(g)}/f^\circ)}{a_{C(s)}(f_{H_2O(g)}/f^\circ)} \tag{1.17.101}$$

In order to calculate the activity of the solid carbon, we start with

$$\left(\frac{\partial\tilde{G}}{\partial P}\right)_T = \left(\frac{\partial\mu}{\partial P}\right)_T = \bar{V} \tag{1.17.102}$$

where

$$\mu = \mu^\circ + RT \ln a \tag{1.17.103}$$

Hence, a change in the molar Gibbs free energy at constant temperature is

$$d\mu = RT d\ln a \tag{1.17.104}$$

Since $d\mu = \bar{V}\, dP = RT d\ln a$, we can write

$$d\ln a = \frac{\bar{V}}{RT} dP \tag{1.17.105}$$

The standard state has $a = 1$, $P = 1\ \mathrm{atm}$, so integrating both sides, we obtain

$$\int_1^a d\ln a' = \int_1^P \frac{\bar{V}}{RT} dP' \tag{1.17.106}$$

$$\ln a = \frac{\bar{V}}{RT}(P-1) \tag{1.17.107}$$

where the assumption that $\bar{V}$ does not change significantly in the solid phase over the pressure range of the integration.

Example 1.17.3

What is $a_{C(s)}$ if the solid phase is coke at $100\ \text{atm}$ and $1000°C$. The density of coke is $1.5\ \text{g/cm}^3$.

Solution

The molar mass of carbon is $12.0107\ \text{g/mol}$. Hence, its molar volume is

$$\bar{V} = \frac{12.0107\ \text{g/mol}}{1.5\ \text{g/cm}^3} = 8.0\ \text{cm}^3/\text{mol} \tag{1.17.108}$$

The pressure $P - 1 = 99\ \text{atm} = 10132500\ \text{Pa}$. Thus,

$$\ln a = \frac{(8.0\ \text{cm}^3/\text{mol})(0.01\ \text{m/cm}^2)}{(8.3144\ \text{J/mol}\cdot\text{K})(1273\ \text{K})}(10132500\ \text{Pa}) \tag{1.17.109}$$

$$= 0.00766 \tag{1.17.110}$$

$$a = 1.01 \tag{1.17.111}$$

showing that the activity of coke is not that different from that of graphite, which we take to be 1.

Recall that for solvated species

$$a = \frac{\gamma c}{c^o} = \gamma c \tag{1.17.112}$$

if $c^o = 1\ \text{M}$ and c is assumed to be expressed in M. The coefficient γ is the activity coefficient. As an example, consider the solubility equilibrium

$$BaF_2(s) \leftrightharpoons Ba^{2+}(aq) + 2F^-(aq) \tag{1.17.113}$$

The activity of $BaF_2(s)$ is 1. Thus, the equilibrium constant, also known as the solubility product, is

$$K_{sp} = a_{Ba^{2+}(aq)} a^2_{F^-(aq)} \tag{1.17.114}$$

The activity coefficient $\gamma_\pm$ is the same for the two aqueous ions, so that

$$K_{sp} = \left(\gamma_\pm [Ba^{2+}]\right)\left(\gamma_\pm [F^-]\right)^2 \tag{1.17.115}$$

$$= [Ba^{2+}][F^-]^2 \gamma_\pm^3 \tag{1.17.116}$$

Therefore,

$$[Ba^{2+}][F^-]^2 = \frac{K_{sp}}{\gamma_\pm^3} \tag{1.17.117}$$

For this reaction $K_{sp} = 1.7 \times 10^{-6}$. On the other hand, the activity coefficient $\gamma_\pm$, from the Debye-Huckel theory, is given by

$$\ln \gamma_\pm = -\frac{1.173\,|z_+ z_-|\sqrt{I_c}}{1+\sqrt{I_c}} \tag{1.17.118}$$

where z_+ and z_- are the charges on the positive and negative ions in units of e, respectively, where e is the fundamental charge on a proton, and

$$I_c = \frac{1}{2}\sum_j z_j^2 c_j \tag{1.17.119}$$

$$= \frac{1}{2}\left(4\left[Ba^{2+}\right] + \left[F^-\right]\right) \tag{1.17.120}$$

If we let $[Ba^{2+}] = s$ and $[F^-] = 2s$, then

$$I_c = \frac{1}{2}(4s + 2s) = 3s \tag{1.17.121}$$

so that the equation for s, which is highly nonlinear, becomes

$$s(2s)^2 e^{-1.173|2\cdot(-1)|\sqrt{3s}/\left(1+\sqrt{3s}\right)} = K_{sp} \tag{1.17.122}$$

Note the similarity to the highly nonlinear relation for partial pressures in non-ideal gas-phase reactions from the last lecture.

How can we solve a highly complex equation of this form? One way is to use an iterative procedure. We start by setting $\gamma_\pm = 1$. This gives us an equation for s that should be reminiscent of the type of calculation used for solubilities in freshman chemistry:

$$s(2s)^2 = 4s^3 = K_{sp} = 1.7 \times 10^{-6} \tag{1.17.123}$$

$$s = \left(\frac{K_{sp}}{4}\right)^{1/3} \tag{1.17.124}$$

$$= \left(\frac{1.7\times10^{-6}}{4}\right)^{1/3} \tag{1.17.125}$$

$$= 7.52 \times 10^{-3}\ \text{M} \tag{1.17.126}$$

We now use this value of s to calculate values for I_c and $\gamma_\pm$:

$$I_c = 3s = 0.0226\ \text{M} \tag{1.17.127}$$

$$\gamma_\pm = e^{-1.172\cdot2\sqrt{0.0226}/\left(1+\sqrt{0.0226}\right)} = 0.736 \tag{1.17.128}$$

We now use this value of $\gamma_\pm$ to calculate a new value for s using

$$s(2s)^2 = \frac{1.7 \times 10^{-6}}{(0.736)^3} \tag{1.17.129}$$

$$4s^3 = \frac{1.7 \times 10^{-6}}{(0.736)^3} \tag{1.17.130}$$

$$s = 0.0102\ \text{M} \tag{1.17.131}$$

We now use this value of s to recalculate I_c and $\gamma_\pm$, and we obtain $\gamma_\pm = 0.705$. Now use this value to recalculate s:

$$4s^3 = \frac{1.7 \times 10^{-6}}{(0.705)^3} \tag{1.17.132}$$

$$s = 0.0107\ \text{M} \tag{1.17.133}$$

which is the converged value. This example illustrates that equilibrium calculations are more complex than what was taught in freshman chemistry due to the fact that activities can, in many instances, make a significant difference.

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1.18: Introduction to Reaction Kinetics - Basic Rate Laws

The kinetic theory of gases can be used to model the frequency of collisions between hard-sphere molecules, which is proportional to the reaction rate. Most systems undergoing a chemical reaction, however, are much more complex. The reaction rates may be dependent on specific interactions between reactant molecules, the phase(s) in which the reaction takes place, etc. The field of chemical kinetics is thus by-and-large based on empirical observations. From experimental observations, scientists have established that reaction rates almost always have a power-law dependence on the concentrations of one or more of the reactants. In the following sections, we will discuss different power laws that are commonly observed in chemical reactions.

0^{th} Order Reaction Kinetics

Consider a closed container initially filled with chemical species A. At $t = 0$, a stimulus, such as a change in temperature, the addition of a catalyst, or irradiation, causes an irreversible chemical reaction to occur in which A transforms into product B:

$$a\mathrm{A} \longrightarrow b\mathrm{B} \tag{1.18.1}$$

The rate that the reaction proceeds, r, can be described as the change in the concentrations of the chemical species with respect to time:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = \frac{1}{b}\frac{d[\mathrm{B}]}{dt} \tag{1.18.2}$$

where $[\mathrm{X}]$ denotes the molar concentration of chemical species X with units of $\frac{\mathrm{mol}}{\mathrm{L}^3}$.

Let us first examine a reaction $\mathrm{A} \longrightarrow \mathrm{B}$ in which the reaction rate, r, is constant with time:

$$r = -\frac{d[\mathrm{A}]}{dt} = k \tag{1.18.3}$$

where k is a constant, also known as the rate constant with units of $\frac{\mathrm{mol}}{\mathrm{m}^3\mathrm{s}}$. Such reactions are called zeroth order reactions because the reaction rate depends on the concentrations of species A and B to the 0^{th} power. Integrating $[\mathrm{A}]$ with respect to T, we find that

$$[\mathrm{A}] = -kt + c_1 \tag{1.18.4}$$

At $t = 0$, $[\mathrm{A}](0) = [\mathrm{A}]_0$. Plugging these values into the equation, we find that $c_1 = [\mathrm{A}]_0$. The final form of the equation is:

$$[\mathrm{A}] = [\mathrm{A}]_0 - kt \tag{1.18.5}$$

A plot of the concentration of species A with time for a 0^{th} order reaction is shown in Figure 1.18.1, where the slope of the line is $-k$ and the y-intercept is $[\mathrm{A}]_0$. Such reactions in which the reaction rates are independent of the concentrations of products and reactants are rare in nature. An example of a system displaying 0^{th} order kinetics would be one in which a reaction is mediated by a catalyst present in small amounts.

1^{st} Order Reaction Kinetics

Experimentally, it is observed than when a chemical reaction is of the form

$$\sum_i \nu_i \mathrm{A}_i = 0 \tag{1.18.6}$$

the reaction rate can be expressed as

$$r = k \prod_{\text{reactants}} [\mathrm{A}_i]^{\nu_i} \tag{1.18.7}$$

where it is assumed that the stoichiometric coefficients ν_i of the reactants are all positive. Thus, or a reaction $\mathrm{A} \longrightarrow \mathrm{B}$, the reaction rate depends on $[\mathrm{A}]$ raised to the first power:

$$r = \frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \tag{1.18.8}$$

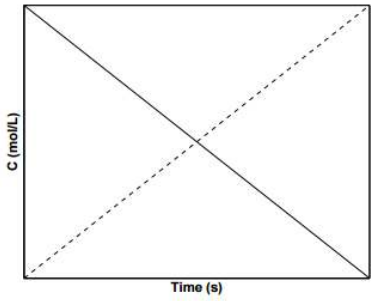


Figure 1.18.1: Plots of [A] (solid line) and [B] (dashed line) over time for a 0^{th} order reaction.

For first order reactions, k has the units of $\frac{1}{\text{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\text{A}] = [\text{A}]_0$, we arrive at the following equation:

$$[\text{A}] = [\text{A}]\, e^{-kt} \tag{1.18.9}$$

Figure 1.18.2 displays the concentration profiles for species A and B for a first order reaction. To determine the value of k from

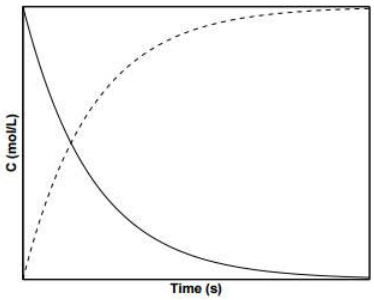


Figure 1.18.2: Plots of [A] (solid line) and [B] (dashed line) over time for a 1^{st} order reaction.

experimental data, it is convenient to take the natural log of Equation 19.8:

$$\ln([\text{A}]) = \ln([\text{A}]_0) - kt \tag{1.18.10}$$

For a first order irreversible reaction, a plot of $\ln([\text{A}])$ vs. t is straight line with a slope of $-k$ and a y-intercept of $\ln([\text{A}]_0)$.

2^{nd} Order Reaction Kinetics

Another type of reaction depends on the square of the concentration of species A - these are known as second order reactions. For a second order reaction in which $2\text{A} \longrightarrow \text{B}$, we can write the reaction rate to be

$$r = -\frac{1}{2}\frac{d[\text{A}]}{dt} = k[\text{A}]^2 \tag{1.18.11}$$

For second order reactions, k has the units of $\frac{\text{m}^3}{\text{mol} \cdot \text{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\text{A}] = [\text{A}]_0$, we arrive at the following equation for the concentration of A over time:

$$[\text{A}] = \frac{1}{2kt + \frac{1}{[\text{A}]_0}} \tag{1.18.12}$$

Figure 1.18.3 shows concentration profiles of A and B for a second order reaction. To determine k from experimental data for

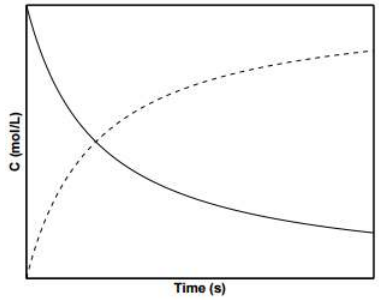


Figure 1.18.3: Plots of [A] (solid line) and [B] (dashed line) over time for a 2^{nd} order reaction.

second-order reactions, it is convenient to invert Equation 19.11:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt \tag{1.18.13}$$

A plot of $1/[A]$ vs. t will give rise to a straight line with slope k and intercept $1/[A]_0$.

Second order reaction rates can also apply to reactions in which two species react with each other to form a product:

$$A + B \xrightarrow{k} C \tag{1.18.14}$$

In this scenario, the reaction rate will depend on the concentrations of both A and B to the first order:

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \tag{1.18.15}$$

In order to integrate the above equation, we need to write it in terms of one variable. Since the concentrations of A and B are related to each other via the chemical reaction equation, we can write:

$$[B] = [B]_0 - ([A]_0 - [A]) = [A] + [B]_0 - [A]_0 \tag{1.18.16}$$

$$\frac{d[A]}{dt} = -k[A]([A] + [B]_0 - [A]_0) \tag{1.18.17}$$

We can then use partial fractions to integrate:

$$kdt = \frac{d[A]}{[A]([A] + [B]_0 - [A]_0)} = \frac{1}{[B]_0 - [A]_0}\left(\frac{d[A]}{[A]} - \frac{d[A]}{[B]_0 - [A]_0 + [A]}\right) \tag{1.18.18}$$

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0} \tag{1.18.19}$$

Figure 1.18.4 displays the concentration profiles of species A, B, and C for a second order reaction in which the initial concentrations of A and B are not equal.

Rate Laws for Elementary Reactions

In general, it is necessary to experimentally measure the concentrations of species over time in order to determine the apparent rate law governing the reaction. If the reactions are elementary reactions, (i.e. they cannot be expressed as a series of simpler reactions), then we can directly define the rate law based on the chemical equation. For example, an elementary

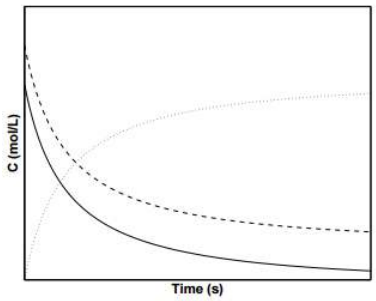


Figure 1.18.4: Plots of [A] (solid line), [B] (dashed line) and [C] (dotted line) over time for a 2^{nd} order reaction in which the initial concentrations of the reactants, $[A]_0$ and $[B]_0$, are not equal.

reaction in which a single reactant transforms into a single product, is unimolecular reaction. These reactions follow 1^{st} order rate kinetics. An example of this type of reaction would be the isomerization of butane:

$$nC_4H_{10} \longrightarrow iC_4H_{10} \tag{1.18.20}$$

From the chemical reaction equation, we can directly write the rate law as

$$\frac{d\left[nC_4H_{10}\right]}{dt} = -k\left[nC_4H_{10}\right] \tag{1.18.21}$$

without the need to carry out experiments.

Elementary bimolecular reactions that involve two molecules interacting to form one or more products follow second order rate kinetics. An example would be the following reaction between a nitrate molecule and carbon monoxide to form nitrogen dioxide and carbon dioxide:

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \tag{1.18.22}$$

For the above elementary reaction, we can directly write the rate law as:

$$\frac{d\left[NO_3\right]}{dt} = -k\left[NO_3\right]\left[CO\right] \tag{1.18.23}$$

Trimolecular elementary reactions involving three reactant molecules to form one or more products are rare due to the low probability of three molecules simultaneously colliding with one another.

Reversible Reactions

Oftentimes, reactions are reversible, meaning that a reaction can proceed in both directions. An example of a reversible reaction is the isomerization of *cis*-1,2-dichloroethene to *trans*-1,2-dichloroethene. At equilibrium, both isomers are present, with their equilibrium concentrations determined by the rate at which the forward and reverse reaction take place.

Consider the following reversible reaction which follows first order rate kinetics in both directions, with rate constants k_1 and k_{-1} in the forward and reverse directions, respectively:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{1.18.24}$$

For the above reaction, we can write rate law for the reaction as:

$$\frac{d\left[\mathrm{A}\right]}{dt} = k_1\left[\mathrm{A}\right] - k_{-1}\left[\mathrm{B}\right] \tag{1.18.25}$$

If the concentration of species $\mathrm{B} = 0$ at the start of the reaction, then we can write:

$$\left[\mathrm{B}\right] = \left[\mathrm{A}\right]_0 - \left[\mathrm{A}\right] \tag{1.18.26}$$

Equation 19.20 then becomes

$$\frac{d\left[\mathrm{A}\right]}{dt} = \left(k_1 + k_{-1}\right)\left[\mathrm{A}\right] - k_{-1}\left[\mathrm{A}\right]_0 \tag{1.18.27}$$

Under equilibrium conditions, $d[\mathrm{A}]/dt = 0$. The equilibrium concentration of species A, $d[\mathrm{A}]_{eq}$, can be calculated from the above expression as

$$[\mathrm{A}]_{eq} = \frac{k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0 \tag{1.18.28}$$

Plugging Equation 19.23 into Equation 19.22 and integrating, we obtain the following expression:

$$[\mathrm{A}] = [\mathrm{A}]_{eq} + c_1 e^{-(k_1+k_{-1})t} \tag{1.18.29}$$

where c_1 is a constant. Applying the initial condition that $[\mathrm{A}] = [\mathrm{A}]_0$ at $t = 0$,

$$[\mathrm{A}] = [\mathrm{A}]_{eq} + \left([\mathrm{A}]_0 - [\mathrm{A}]_{eq}\right) e^{-(k_1+k_{-1})t} \tag{1.18.30}$$

From Equation 19.20, we can also write an expression for the equilibrium constant, K_c

$$\frac{[\mathrm{B}]_{eq}}{[\mathrm{A}]_{eq}} = \frac{k_1}{k_{-1}} = K_{eq} \tag{1.18.31}$$

In general, the equilibrium constant K_c is equal to the ratio of the forward and reverse rate constants. Consider the following bimolecular elementary reaction:

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} + \mathrm{D} \tag{1.18.32}$$

The forward and reverse reaction rates will be

$$r_{forward} = k_1 [\mathrm{A}] [\mathrm{B}] \tag{1.18.33}$$

$$r_{reverse} = k_{-1} [\mathrm{C}] [\mathrm{D}] \tag{1.18.34}$$

At equilibrium, $r_{forward} = r_{reverse}$, so

$$k_1 [\mathrm{A}]_{eq} [\mathrm{B}]_{eq} = k_{-1} [\mathrm{C}]_{eq} [\mathrm{D}]_{eq} \tag{1.18.35}$$

The equilibrium constant, K_c is given by

$$K_c = \frac{[\mathrm{C}]_{eq} [\mathrm{D}]_{eq}}{[\mathrm{A}]_{eq} [\mathrm{B}]_{eq}} \tag{1.18.36}$$

Plugging in Equation 19.30 into Equation 19.31, we arrive at

$$K_c = \frac{k_1}{k_{-1}} \tag{1.18.37}$$

The above equation is true for all reversible elementary reactions.

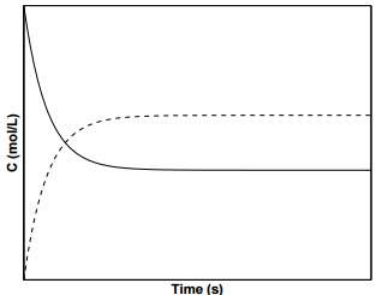


Figure 1.18.5: Plots of [A] (solid line) and [B] (dashed line) over time for a reversible reaction in which the forward and reverse reactions follow first order rate kinetics, with $k_1 > k_{-1}$

Relaxation Method to Determine Rate Constants

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the

temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. Consider the following reversible reaction:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{1.18.38}$$

The rate law can be written as

$$\frac{d\left[\mathrm{B}\right]}{dt} = k_1\left[\mathrm{A}\right] - k_{-1}\left[\mathrm{B}\right] \tag{1.18.39}$$

Consider a system comprising A and B that is allowed to achieve equilibrium concentrations at a temperature, T_1. After equilibrium is achieved, the temperature of the system is instantaneously lowered to T_2 and the system is allowed to achieve new equilibrium concentrations of A and B, $\left[\mathrm{A}\right]_{\mathrm{eq},2}$ and $\left[\mathrm{B}\right]_{\mathrm{eq},2}$. During the transition time from the first equilibrium state to the second equilibrium state, we can write the instantaneous concentration of A as

$$\left[\mathrm{A}\right] = \left[\mathrm{B}\right]_{\mathrm{eq},1} - \left[\mathrm{B}\right] \tag{1.18.40}$$

The rate of change of species B can then be written as

$$\frac{d\left[\mathrm{B}\right]}{dt} = k_1\left(\left[\mathrm{B}\right]_{\mathrm{eq},1} - \left[\mathrm{B}\right]\right) - k_{-1}\left[\mathrm{B}\right] = k_1\left[\mathrm{B}\right]_{\mathrm{eq},1} - \left(k_1 + k_{-1}\right)\left[\mathrm{B}\right] \tag{1.18.41}$$

At equilibrium, $d\left[\mathrm{B}\right]/dt = 0$ and $\left[\mathrm{B}\right] = \left[\mathrm{B}\right]_{\mathrm{eq},2}$, allowing us to write

$$k_1\left[\mathrm{B}\right]_{\mathrm{eq},1} = \left(k_1 + k_{-1}\right)\left[\mathrm{B}\right]_{\mathrm{eq},2} \tag{1.18.42}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathrm{B}}{\left(\left[\mathrm{B}\right]_{\mathrm{eq},2} - \left[\mathrm{B}\right]\right)} = \left(k_1 + k_{-1}\right)dt \tag{1.18.43}$$

Integrating yields

$$-\ln\left(\left[\mathrm{B}\right] - \left[\mathrm{B}\right]_{\mathrm{eq},2}\right) = -\left(k_1 + k_{-1}\right)t + C \tag{1.18.44}$$

We can rearrange the above equation in terms of B

$$\left[\mathrm{B}\right] = Ce^{-(k_1+k_{-1})t} + \left[\mathrm{B}\right]_{\mathrm{eq},2} \tag{1.18.45}$$

At $t = 0$, $\left[\mathrm{B}\right] = \left[\mathrm{B}\right]_{\mathrm{eq},1}$, so $C = \left[\mathrm{B}\right]_{\mathrm{eq},1} - \left[\mathrm{B}\right]_{\mathrm{eq},2}$. Plugging the the value of C, we arrive at

$$\left[\mathrm{B}\right] - \left[\mathrm{B}\right]_{\mathrm{eq},2} = \left(\left[\mathrm{B}\right]_{\mathrm{eq},1} - \left[\mathrm{B}\right]_{\mathrm{eq},2}\right)e^{-(k_1+k_{-1})t} \tag{1.18.46}$$

which can also be expressed as

$$\Delta\left[\mathrm{B}\right] = \Delta\left[\mathrm{B}\right]_0 e^{-(k_1+k_{-1})t} = \Delta\left[\mathrm{B}\right]_0 e^{-t/\tau} \tag{1.18.47}$$

where $\Delta\left[\mathrm{B}\right]$ is the difference in the concentration of B from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta\left[\mathrm{B}\right]/\Delta\left[\mathrm{B}\right]_0\right)$ versus t will be linear with a slope of $-\left(k_1 + k_{-1}\right)$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

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1.19: Collision theory, transition state theory, and the prediction of rate laws and rate constants

Rate Law and Collision Theory

Consider the reaction

$$\mathbf{A} + \mathbf{B} \longrightarrow \mathbf{C} \tag{1.19.1}$$

In the last class, we regarded the rate law

$$r = k\,[\mathbf{A}]\,[\mathbf{B}] \tag{1.19.2}$$

as empirical. As it happens, we can actually derive this using the collision theory discussed in Lecture 6. Recall, from lecture 6, that the collision rate between two atoms or molecules in a system is

$$\gamma = \rho\sigma\,\langle|\mathbf{v}|\rangle \tag{1.19.3}$$

where ρ is the number density, σ is the collision cross section, and $\langle|\mathbf{v}|\rangle$ is the relative velocity between the two atoms or molecules. Now, if the two colliding atoms or molecules are different, and we are interested in the rate of collisions of atoms/molecules of type $\mathbf{A}$ with those of type $\mathbf{B}$, then the collision rate must be written as

$$\gamma_{\mathbf{AB}} = \sigma_{\mathbf{AB}}\,\langle|\mathbf{v}_{\mathbf{AB}}|\rangle\,\rho_{\mathbf{B}} \tag{1.19.4}$$

Here $\rho_{\mathbf{B}}$ is the density of atoms/molecules of type $\mathbf{B}$, $|\mathbf{v}_{\mathbf{AB}}| = |\mathbf{v}_{\mathbf{B}} - \mathbf{v}_{\mathbf{A}}|$ is the relative speed between $\mathbf{A}$ and $\mathbf{B}$, and $\sigma_{\mathbf{AB}}$ is the cross section between $\mathbf{A}$ and $\mathbf{B}$, which, is given the average of arithmetic and geometric averages:

$$\sigma_{\mathbf{AB}} = \frac{1}{2}\left[\left(\frac{\sigma_{\mathbf{A}} + \sigma_{\mathbf{B}}}{2}\right) + \sqrt{\sigma_{\mathbf{A}}\sigma_{\mathbf{B}}}\right] \tag{1.19.5}$$

From the Maxwell-Boltzmann distribution,

$$\langle|\mathbf{v}_{\mathbf{AB}}|\rangle = \sqrt{\frac{8k_BT}{\pi\mu}} \tag{1.19.6}$$

where the reduced mass

$$\mu = \frac{m_{\mathbf{A}}m_{\mathbf{B}}}{m_{\mathbf{A}} + m_{\mathbf{B}}} \tag{1.19.7}$$

The collision rate $\gamma_{\mathbf{AB}}$ is the rate for the collision of one atom/molecule of $\mathbf{A}$. If there are $N_{\mathbf{A}}$ atoms/molecules of $\mathbf{A}$, then the total collision rate for $\mathbf{A}$ with $\mathbf{B}$ is

$$\gamma_{\text{tot}} = N_{\mathbf{A}}\gamma_{\mathbf{AB}} = N_{\mathbf{A}}\sigma_{\mathbf{AB}}\,\langle|\mathbf{v}_{\mathbf{AB}}|\rangle\,\rho_{\mathbf{B}} \tag{1.19.8}$$

However, the number density of $\mathbf{A}$ is $\rho_{\mathbf{A}} = N_{\mathbf{A}}/V$, so we can write the total collision rate as

$$\gamma_{\text{tot}} = \sigma_{\mathbf{AB}}V\,\langle|\mathbf{v}_{\mathbf{AB}}|\rangle\,\rho_{\mathbf{A}}\rho_{\mathbf{B}} \tag{1.19.9}$$

In a time interval dt, the number of collisions dN_{coll} is

$$dN_{\text{coll}} = \gamma_{\text{tot}}dt = \sigma_{\mathbf{AB}}V\,\langle|\mathbf{v}_{\mathbf{AB}}|\rangle\,\rho_{\mathbf{A}}\rho_{\mathbf{B}}dt \tag{1.19.10}$$

Let P_{rxn} denote the probability that a collision between $\mathbf{A}$ and $\mathbf{B}$ leads to product $\mathbf{C}$. The rate of decrease of $N_{\mathbf{A}}$ must then be

$$dN_{\mathbf{A}} = -P_{\text{rxn}}dN_{\text{coll}} = -\sigma_{\mathbf{AB}}P_{\text{rxn}}V\,\langle|\mathbf{v}_{\mathbf{AB}}|\rangle\,\rho_{\mathbf{A}}\rho_{\mathbf{B}}dt \tag{1.19.11}$$

so that

$$\frac{dN_{\mathbf{A}}}{dt} = -\sigma_{\mathbf{AB}}P_{\text{rxn}}V\,\langle|\mathbf{v}_{\mathbf{AB}}|\rangle\,\rho_{\mathbf{A}}\rho_{\mathbf{B}} \tag{1.19.12}$$

Note that the rate is

$$r = -\frac{d[\mathrm{A}]}{dt} \tag{1.19.13}$$

However, $[\mathrm{A}]$ is in units of moles/liter. The ratio $N_\mathrm{A}/(N_0 V)$, where N_0 is Avogadro's number, has the proper units of moles/liter, if V is in liters. Thus,

$$\frac{d[\mathrm{A}]}{dt} = \frac{d(N_\mathrm{A}/(N_0 V))}{dt} \tag{1.19.14}$$

$$= -\frac{1}{N_0 V}\sigma_{\mathrm{AB}} P_{\mathrm{rxn}} V \langle|\mathrm{v}_{\mathrm{AB}}|\rangle \rho_\mathrm{A}\rho_\mathrm{B} \tag{1.19.15}$$

$$= -\sigma_{\mathrm{AB}} P_{\mathrm{rxn}} N_0^{-1} \langle|\mathrm{v}_{\mathrm{AB}}|\rangle \rho_\mathrm{A}\rho_\mathrm{B} \tag{1.19.16}$$

Since ρ_A has units of (molecules of A/liters), we can write $\rho_\mathrm{A} = N_0[\mathrm{A}]$, and similarly, $\rho_\mathrm{B} = N_0[\mathrm{B}]$. This gives

$$\frac{d[\mathrm{A}]}{dt} = -\sigma_{\mathrm{AB}} P_{\mathrm{rxn}} N_0 \langle|\mathrm{v}_{\mathrm{AB}}|\rangle [\mathrm{A}][\mathrm{B}] = -k[\mathrm{A}][\mathrm{B}] \tag{1.19.17}$$

where the rate constant is

$$k = \sigma_{\mathrm{AB}} P_{\mathrm{rxn}} N_0 \langle|\mathrm{v}_{\mathrm{AB}}|\rangle \tag{1.19.18}$$

To determine the reaction probability P_{rxn}, consider the energy profile for the reaction in Figure 1.19.1. In the gas phase, the activation "energy", denote E_a in the figure is the potential energy at the top of the hill, which we denote as $\mathcal{E}^\ddagger$. If the reaction takes place in a condensed phase, such as in solution, then the activation "energy" is the free energy $\Delta G^\ddagger$.

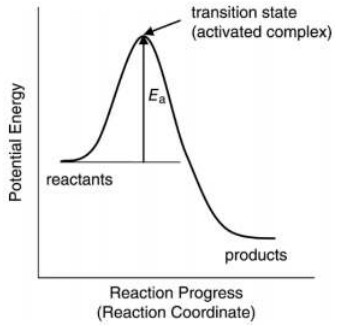


Figure 1.19.1: Illustration of a reaction energy profile.

If A and B are atoms, then P_{rxn} is the probability that the energy E_{AB} between A and B must be larger than this energy E_a in order for the collision to yield product C. If A and B are molecules, then A and B must also have the right orientation in addition to a sufficiently high energy. The probability that they have the right orientation is a fraction $f < 1$, which we call the steric factor. When A and B are atoms, $f = 1$. Generally, we can write

$$P_{\mathrm{rxn}} = fP(E_{\mathrm{AB}} > E_a) \tag{1.19.19}$$

The general probability distribution $p(E_{\mathrm{AB}})$ is just given by the Boltzmann distribution

$$p(E_{\mathrm{AB}})\, Ce^{-\beta E_{\mathrm{AB}}} \tag{1.19.20}$$

where C is a normalization constant. The normalization condition is

$$\int_0^\infty p(E_{\mathrm{AB}})\, dE_{\mathrm{AB}} = C\int_0^\infty e^{-\beta E_{\mathrm{AB}}} = -\frac{C}{\beta}e^{-\beta E_{\mathrm{AB}}}\Big|_0^\infty = 1 \tag{1.19.21}$$

which gives $C = \beta = 1/(k_B T)$. Thus,

$$p(E_{\mathrm{AB}}) = \beta e^{-\beta E_{\mathrm{AB}}} \tag{1.19.22}$$

Now, the probability $P(E_{\mathrm{AB}} > E_a)$ that $E_{\mathrm{AB}} > E_a$ is

$$P(E_{\mathrm{AB}} > E_a) = \beta\int_{E_a}^\infty e^{-\beta E_{\mathrm{AB}}} dE_{\mathrm{AB}} = e^{-\beta E_a} \tag{1.19.23}$$

which gives the rate constant as

$$k = \sigma_{AB} N_0 f e^{-\beta E_a} \langle |v_{AB}| \rangle = \sigma_{AB} N_0 f e^{-\beta E_a} \left(\frac{8}{\beta \pi \mu} \right)^{1/2} \tag{1.19.24}$$

We see, generally, that

$$k = A e^{-\beta E_a} \tag{1.19.25}$$

where E_a is the activation potential $\mathcal{E}^\ddagger$ in the gas phase and the activation free energy $\Delta G^\ddagger$ in condensed phases. This is known as the *Arrhenius law*.

Note that if we plot $\ln k$ vs. $1/T$, which is given by

$$\ln k = \ln A - \frac{E_a}{k_B T} \tag{1.19.26}$$

the plot will be a line with slope $-E_a/k_B$. Such a plot is called an Arrhenius plot. Note, moreover, that if A and B are the same atom or molecule type, then the rate law we derived, would take the form of a second-order rate law

$$\frac{d[A]}{dt} = -k[A]^2 \tag{1.19.27}$$

Transition State Theory

In Figure 1.19.1, the point at which we evaluate or measure E_a serves as a dividing line (also called a *dividing surface*) between reactants and products. At this point, we do not have $A + B$, and we do not have C. Rather, what we have is an activated complex of some kind called a *transition state* between reactants and products. The value of the reaction coordinate at the transition state is denoted $q^\ddagger$. Recall our notation x for the complete set of coordinates and momenta of all of the atoms in the system. Generally, the reaction coordinate q is a function $q(x)$ of all of the coordinates and momenta, although typically, $q(x)$ is a function of a subset of the coordinates and, possibly, the momenta.

As an example, let us consider two atoms A and B undergoing a collision. An appropriate reaction coordinate could simply be the distance r between A and B. This distance is a function of the positions r_A and r_B of the two atoms, in that

$$q = r = |r_A - r_B| \tag{1.19.28}$$

When A and B are molecules, such as proteins, $q(x)$ is a much more complicated function of x.

Now, recall that the mechanical energy $\mathcal{E}(x)$ is given by

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{p_i^2}{2m_1} + U(r_1, \ldots, r_N) \tag{1.19.29}$$

and is a sum of kinetic and potential energies. Transition state theory assumes the following:

1. We start a trajectory obeying this equation of motion with an initial condition x that makes $q(x) = q^\ddagger$ and such that $\dot{q}(x) > 0$ so that the reaction coordinate proceeds initial to the right, i.e., toward products.
2. We follow the motion x_t of the coordinates and momenta in time starting from this initial condition x, which gives us a unique function $x_t(x)$.
3. If $q(x_t(x)) > q^\ddagger$ at time t, then the trajectory is designated as "reactive" and contributes to the reaction rate.

Define a function $\theta(y)$, which is 1 if $y \geq 0$ and 0 if $y < 0$. The function $\theta(y)$ is known as a *step function*.

We now define a *flux* of reactive trajectories $k(t)$ using statistical mechanics

$$k(t) = \frac{1}{hQ_r} \int_{q(x)=q^\ddagger} dx\, e^{-\beta \mathcal{E}(x)} |\dot{q}(x)| \theta(q(x_t(x)) - q^\ddagger) \tag{1.19.30}$$

where h is Planck's constant. Here Q_r is the partition function of the reactants

$$Q_r = \int dx\, e^{-\beta \mathcal{E}(x)} \theta(q^\ddagger - q(x)) \tag{1.19.31}$$

The meaning of Equation 1.19.30 is an ensemble average over a canonical ensemble of the product $|\dot{q}(\mathbf{x})|$ and $\theta\left(q\left(\mathbf{x}_t\left(\mathbf{x}\right)\right)-q^{\ddagger}\right)$. The first factor in this product $|\dot{q}(\mathbf{x})|$ forces the initial velocity of the reaction coordinate to be positive, i.e., toward products, and the step function $\theta\left(q\left(\mathbf{x}_t\left(\mathbf{x}\right)\right)-q^{\ddagger}\right)$ requires that the trajectory of $q\left(\mathbf{x}_t\left(\mathbf{x}\right)\right)$ be reactive, otherwise, the step function will give no contribution to the flux. The function $k(t)$ in Equation 1.19.30 is known as the *reactive flux*. In the definition of Q_r the step function $\theta\left(q^{\ddagger}-q\left(\mathbf{x}\right)\right)$ measures the total number of microscopic states on the reactive side of the energy profile.

A plot of some examples of reactive flux functions $k(t)$ is shown in Figure **1.19.2**. These functions are discussed in greater detail in *J. Chem. Phys.* **95**, 5809 (1991). These examples all show that $k(t)$ decays at first but then finally reaches a plateau value. This plateau value is taken to be the true rate of the reaction under the assumption that eventually, all trajectories that will become reactive will have done so after a sufficiently long time. Thus,

$$k=\lim_{t\to\infty}k\left(t\right) \tag{1.19.32}$$

gives the true rate constant. On the other hand, a common approximation is to take the value $k(0)$ as an estimate of the rate constant, and this is known as the transition *state theory approximation* to k, i.e.,

$$k^{(\mathrm{TST})}=k\left(0\right) \tag{1.19.33}$$

$$=\frac{1}{Q_r}\int_{q(\mathbf{x})=q^{\ddagger}}d\mathbf{x}\,e^{-\beta\mathcal{E}(\mathbf{x})}\left|\dot{q}\left(\mathbf{x}\right)\right|\theta\left(q\left(\mathbf{x}\right)-q^{\ddagger}\right) \tag{1.19.34}$$

However, note that since we require $\dot{q}(\mathbf{x})$ to initially be toward products, then by definition, at $t=0$, $q(\mathbf{x})\geq q^{\ddagger}$, and the step function in the above expression is redundant. In addition, if $\dot{q}(\mathbf{x})$ only depends on momenta (or velocities) and not actually on coordinates, which will be true if $q(\mathbf{x})$ is not curvilinear (and is true for some curvilinear coordinates $q(\mathbf{x})$), and if $q(\mathbf{x})$ only depends on coordinates, then Equation ??? reduces to

$$k^{(\mathrm{TST})}=\frac{1}{hQ_r}\int d\mathbf{x}_{\mathbf{p}}e^{-\beta\sum_{i=1}^{N}\mathbf{p}_i^2/2m_i}\left|\dot{q}\left(\mathbf{p}_1,\ldots,\mathbf{p}_N\right)\right|\int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^{\ddagger}}d\mathbf{x}_{\mathbf{r}}e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{1.19.35}$$

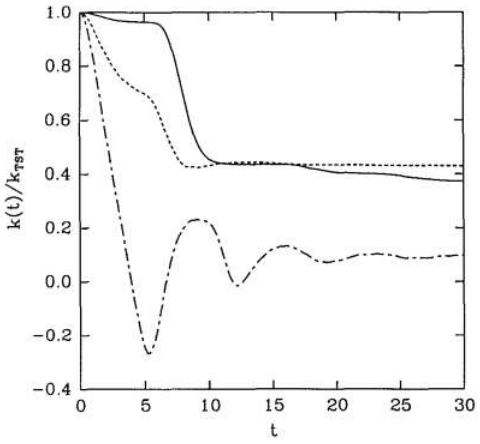


Figure **1.19.2**: Examples of the reactive flux $k(t)$.

The integral

$$Z^{\ddagger}=\int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^{\ddagger}}d\mathbf{x}_{\mathbf{r}}e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{1.19.36}$$

counts the number of microscopic states consistent with the condition $q\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right)=q^{\ddagger}$ and is, therefore, a kind of partition function, and is denoted $Q^{\ddagger}$. On the other hand, because it is a partition function, we can derive a free energy $\Delta F^{\ddagger}$ from it

$$F^{\ddagger}\propto -k_BT\ln Z^{\ddagger} \tag{1.19.37}$$

Similarly, if we divide Q_r into its ideal-gas and configurational contributions

$$Q_r=Q_r^{(\mathrm{ideal})}Z_r \tag{1.19.38}$$

then we can take

$$Z_r = e^{-\beta F_r} \tag{1.19.39}$$

where F_r is the free energy of the reactants. Finally, setting $\dot{q} = p/\mu$, where μ is the associated mass, and p is the corresponding momentum of the reaction coordinate, then, canceling most of the momentum integrals between the numerator and $Q_r^{(\text{ideal})}$, the momentum integral we need is

$$\int_0^\infty e^{-\beta p^2/2\mu} \frac{p}{\mu} = k_B T \tag{1.19.40}$$

which gives the final expression for the transition state theory rate constant

$$k^{(\text{TST})} = \frac{k_B T}{h} e^{-\beta(F^\ddagger - F_r)} = \frac{k_B T}{h} e^{-\beta \Delta F^\ddagger} \tag{1.19.41}$$

Figure 1.19.2 actually shows $k(t)/k^{(\text{TST})}$, which must start at 1. As the figure shows, in addition, for $t > 0$, $k(t) < k^{(\text{TST})}$. Hence, $k^{(\text{TST})}$ is always an upper bound to the true rate constant. Transition state theory assumes that any trajectory that initially moves toward products will be a reactive trajectory. For this reason, it overestimates the reaction rate. In reality, trajectories can cross the dividing surface several or many times before eventually proceeding either toward products *or* back toward reactants.

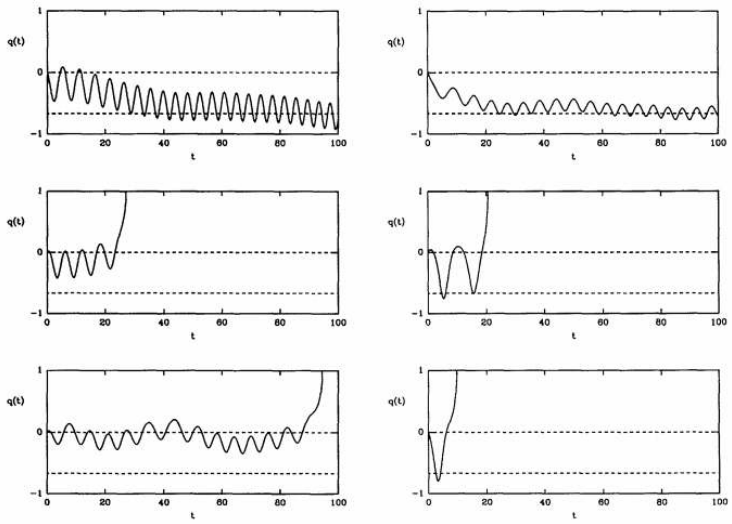


Figure 1.19.3: Examples of the trajectories in a typical system, some of which are reactive but some of which return to reactants.

Figure 1.19.3 shows that one can obtain trajectories of both types. Here, the dividing surface lies at $q = 0$. Left, toward $q = -1$ is the reactant side, and right, toward $q = 1$ is the product side. Because some trajectories return to reactants and never become products, the true rate is always less than $k^{(\text{TST})}$, and we can write

$$k = \kappa k^{(\text{TST})} \tag{1.19.42}$$

where the factor $\kappa < 1$ is known as the *transmission factor*. This factor accounts for multiple recrossings of the dividing surface and the fact that some trajectories do not become reactive ones.

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1.20: Complex reaction mechanisms

A major goal in chemical kinetics is to determine the sequence of elementary reactions, or the reaction mechanism, that comprise complex reactions. For example, Sherwood Rowland and Mario Molina won the Nobel Prize in Chemistry in 1995 for proposing the elementary reactions involving chlorine radicals that contribute to the overall reaction of $O_3 \rightarrow O_2$ in the troposphere. In the following sections, we will derive rate laws for complex reaction mechanisms, including reversible, parallel and consecutive reactions.

Parallel Reactions

Consider the reaction in which chemical species $\mathbf{A}$ undergoes one of two irreversible first order reactions to form either species $\mathbf{B}$ or species $\mathbf{C}$:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{1.20.1}$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{C} \tag{1.20.2}$$

The overall reaction rate for the consumption of $\mathbf{A}$ can be written as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] - k_2[\mathrm{A}] = -(k_1 + k_2)[\mathrm{A}] \tag{1.20.3}$$

Integrating $[\mathrm{A}]$ with respect to t, we obtain the following equation:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{1.20.4}$$

Plugging this expression into the equation for $\frac{d[\mathrm{B}]}{dt}$, we obtain:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{1.20.5}$$

Integrating $[\mathrm{B}]$ with respect to t, we obtain:

$$[\mathrm{B}] = -\frac{k_1[\mathrm{A}]_0}{k_1 + k_2}\left(e^{-(k_1+k_2)t}\right) + c_1 \tag{1.20.6}$$

At $t = 0$, $[\mathrm{B}] = 0$. Therefore,

$$c_1 = \frac{k_1[\mathrm{A}]_0}{k_1 + k_2} \tag{1.20.7}$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{1.20.8}$$

Likewise,

$$[\mathrm{C}] = \frac{k_2[\mathrm{A}]_0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{1.20.9}$$

The ratio of $[\mathrm{B}]$ to $[\mathrm{C}]$ is simply:

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2} \tag{1.20.10}$$

An important parallel reaction in industry occurs in the production of ethylene oxide, a reagent in many chemical processes and also a major component in explosives. Ethylene oxide is formed through the partial oxidation of ethylene:

$$2\,C_2H_4 + O_2 \xrightarrow{k_1} 2\,C_2H_4O \tag{1.20.11}$$

However, ethylene can also undergo a combustion reaction:

$$C_2H_4 + 3\,O_2 \xrightarrow{k_2} 2\,CO_2 + 2\,H_2O \tag{1.20.12}$$

To select for the first reaction, the oxidation of ethylene takes place in the presence of a silver catalyst, which significantly increases k_1 compared to k_2. Figure 1.20.1 displays the concentration profiles for species A, B, and C in a parallel reaction in which $k_1 > k_2$.

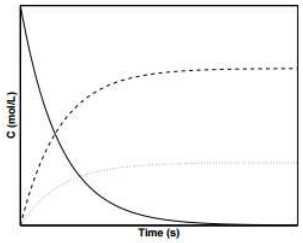


Figure 1.20.1: Plots of [A] (solid line), [B] (dashed line) and [C] (dotted line) over time for a parallel reaction.

Consecutive Reactions

Consider the following series of first-order irreversible reactions, where species A reacts to form an intermediate species, I, which then reacts to form the product, P:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.20.13}$$

We can write the reaction rates of species A, I and P as follows:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] \tag{1.20.14}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{I}] \tag{1.20.15}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{1.20.16}$$

As before, integrating [A] with respect to t leads to:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{1.20.17}$$

The concentration of species I can be written as

$$[\mathrm{I}] = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{1.20.18}$$

Then, solving for [P], we find that:

$$[\mathrm{P}] = [\mathrm{A}]_0\left[1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right] \tag{1.20.19}$$

Figure 1.20.2 displays the concentration profiles for species A, I, and P in a consecutive reaction in which $k_1 = k_2$. As can be seen from the figure, the concentration of species I reaches a maximum at some time, t_{max}. Oftentimes, species I is the desired product. Returning to the oxidation of ethylene into ethylene oxide, it is important to note another reaction in which ethylene oxide can decompose into carbon dioxide and water through the following reaction

$$C_2H_4O + \frac{5}{2}O_2 \xrightarrow{k_3} 2\,CO_2 + 2\,H_2O \tag{1.20.20}$$

Thus, to maximize the concentration of ethylene oxide, the oxidation of ethylene is only allowed proceed to partial completion before the reaction is stopped.

Finally, in the limiting case when $k_2 \gg k_1$, we can write the concentration of P as

$$[\mathrm{P}] \approx [\mathrm{A}]_0\left\{1 + \frac{1}{-k_2}k_2 e^{-k_1 t}\right\} = [\mathrm{A}]_0\left(1 - e^{-k_1 t}\right) \tag{1.20.21}$$

Thus, when $k_2 \gg k_1$, the reaction can be approximated as $\mathrm{A} \rightarrow \mathrm{P}$ and the apparent rate law follows 1^{st} order kinetics.

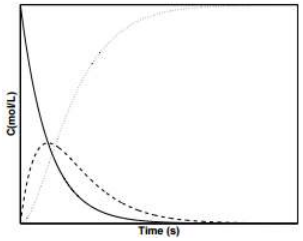


Figure 1.20.2: Plots of [A] (solid line), [I] (dashed line) and [P] (dotted line) over time for consecutive first order reactions.

Consecutive Reactions With an Equilibrium

Consider the reactions

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.20.22}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{1.20.23}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{1.20.24}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{1.20.25}$$

The exact solutions of these is straightforward, in principle, but rather involved, so we will just state the exact solutions, which are

$$[\mathrm{A}](t) = \frac{[\mathrm{A}]_0}{2\lambda}\left[(\lambda - k_1 + K)\, e^{-(k_1+K-\lambda)t/2} + (\lambda + k_1 - K)\, e^{-(k_1+K+\lambda)t/2}\right] \tag{1.20.26}$$

$$[\mathrm{I}](t) = \frac{k_1[\mathrm{A}]_0}{\lambda}\left[e^{-(k_1+K-\lambda)t/2} - e^{-(k_1+K+\lambda)t/2}\right] \tag{1.20.27}$$

$$[\mathrm{P}](t) = 2k_1k_2[\mathrm{A}]_0\left[\frac{2}{(k_1+K)^2-\lambda^2} - \frac{1}{\lambda}\left(\frac{e^{-(k_1+K-\lambda)t/2}}{k_1+K-\lambda} - \frac{e^{-(k_1+K+\lambda)t/2}}{k_1+K+\lambda}\right)\right] \tag{1.20.28}$$

where

$$K = k_2 + k_{-1} \tag{1.20.29}$$

$$\lambda = \sqrt{(k_1-K)^2 - 4k_1k_{-1}} \tag{1.20.30}$$

Steady-State Approximations

Consider the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.20.31}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{1.20.32}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{1.20.33}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{1.20.34}$$

These equations can be solved explicitly in terms of [A], [I], and [P], but the math becomes very complicated quickly. If, however, $k_2 + k_{-1} \gg k_1$ (in other words, the rate of consumption of I is much faster than the rate of production of I), we can make the approximation that the concentration of the intermediate species, I, is small and constant with time:

$$\frac{d[\mathrm{I}]}{dt} \approx 0 \tag{1.20.35}$$

Equation 21.22 can now be written as

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}]_{ss} - k_2[\mathrm{I}]_{ss} \approx 0 \tag{1.20.36}$$

where $[\mathrm{I}]_{ss}$ is a constant represents the steady state concentration of intermediate species, $[\mathrm{I}]$. Solving for $[\mathrm{I}]_{ss}$,

$$[\mathrm{I}]_{ss} = \frac{k_1}{k_{-1} + k_2}[\mathrm{A}] \tag{1.20.37}$$

We can then write the rate equation for species $\mathbf{A}$ as

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}]_{ss} = -k_1[\mathrm{A}] + k_{-1}\frac{k_1}{k_{-1} + k_2}[\mathrm{A}] = -\frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{A}] \tag{1.20.38}$$

Integrating,

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-\frac{k_1 k_2}{k_{-1} + k_2}t} \tag{1.20.39}$$

Equation 21.28 is the same equation we would obtain for apparent 1^{st} order kinetics of the following reaction:

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{1.20.40}$$

where

$$k' = \frac{k_1 k_2}{k_{-1} + k_2} \tag{1.20.41}$$

Figure **1.20.3** displays the concentration profiles for species, **A**, **I**, and **P** with the condition that $k_2 + k_{-1} \gg k_1$. These types of reaction kinetics appear when the intermediate species, **I**, is highly reactive.

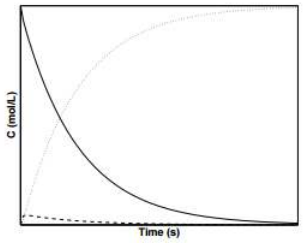


Figure **1.20.3**: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for $k_2 + k_{-1} \gg k_1$.

Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN \tag{1.20.42}$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1^{st} order rate kinetics. Experimentally, however, 1^{st} order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2^{nd} order rate law:

$$\frac{d[CH_3NC]}{dt} = -k[CH_3NC]^2 \tag{1.20.43}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{1.20.44}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{1.20.45}$$

where $\mathbf{M}$ can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of $\mathbf{A}^*$ is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species $\mathbf{B}$ with time:

$$\frac{d[\mathrm{A}^*]}{dt} = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}[\mathrm{A}^*]_{ss}[\mathrm{M}] - k_2[\mathrm{A}^*]_{ss} \approx 0 \tag{1.20.46}$$

Solving for $[\mathrm{A}^*]$,

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{1.20.47}$$

The reaction rates of species $\mathbf{A}$ and $\mathbf{B}$ can be written as

$$-\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = k_2[\mathrm{A}^*] = \frac{k_1 k_2[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} = k_{\mathrm{obs}}[\mathrm{A}] \tag{1.20.48}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{1.20.49}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}[\mathrm{M}] \gg k_2$. Equation 21.33 then becomes

$$-\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{1.20.50}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}[\mathrm{M}] \ll k_2$. In this scenario, equation 21.33 becomes

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}] \tag{1.20.51}$$

which follows second order rate kinetics, consistent with experimental observations.

Equilibrium Approximations

Consider again the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.20.52}$$

Now let us consider the situation in which $k_2 \ll k_1$ and k_{-1}. In other words, the conversion of $\mathbf{I}$ to $\mathbf{P}$ is slow and is the *rate-limiting step*. In this situation, we can assume that $[\mathrm{A}]$ and $[\mathrm{I}]$ are in equilibrium with each other. As we derived before for a reversible reaction in equilibrium,

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} \approx \frac{[\mathrm{I}]}{[\mathrm{A}]} \tag{1.20.53}$$

or, in terms of $[\mathrm{I}]$,

$$[\mathrm{I}] = K_{\mathrm{eq}}[\mathrm{A}] \tag{1.20.54}$$

These conditions also result from the exact solution when we set $k_2 \approx 0$. When this is done, we have the approximate expressions from the exact solution:

$$K \approx k_{-1} \tag{1.20.55}$$

$$\lambda \approx \sqrt{\left(k_1 - k_{-1}\right)^2 + 4k_1k_{-1}} = \sqrt{k_1^2 + 2k_1k_{-1} + k_{-1}^2} = k_1 + k_{-1} \tag{1.20.56}$$

$$\lambda - k_1 + K \approx k_1 + k_{-1} + k_1 - k_{-1} = 2k_1 \tag{1.20.57}$$

$$\lambda + k_1 - K \approx k_1 + k_{-1} + k_1 - k_{-1} = 2k_1 \tag{1.20.58}$$

$$k_1 + K - \lambda \approx k_1 + k_{-1} - k_1 - k_{-1} = 0 \tag{1.20.59}$$

$$k_1 + K + \lambda \approx k_1 + k_{-1} + k_1 + k_{-1} = 2\left(k_1 + k_{-1}\right) \tag{1.20.60}$$

and the approximate solutions become

$$[\mathrm{A}](t) = \frac{[\mathrm{A}]_0}{2\left(k_1 + k_{-1}\right)}\left[2k_{-1} + 2k_1 e^{-\left(k_1 + k_{-1}\right)t}\right] \tag{1.20.61}$$

$$[\mathrm{I}](t) = \frac{k_1[\mathrm{A}]_0}{\left(k_1 + k_{-1}\right)}\left[1 - e^{-\left(k_1 + k_{-1}\right)t}\right] \tag{1.20.62}$$

In the long-time limit, when equilibrium is reached and transient behavior has decayed away, we find

$$\frac{[\mathrm{I}]}{[\mathrm{A}]} \equiv K_{\mathrm{eq}} \rightarrow \frac{k_1}{k_{-1}} \tag{1.20.63}$$

Plugging the above equation into the expression for $d[\mathrm{P}]/dt$,

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] = k_2K_{\mathrm{eq}}[\mathrm{A}] = \frac{k_1k_2}{k_{-1}}[\mathrm{A}] \tag{1.20.64}$$

The reaction can thus be approximated as a 1^{st} order reaction

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{1.20.65}$$

with

$$k' = \frac{k_1k_2}{k_{-1}} \tag{1.20.66}$$

Figure 1.20.4 displays the concentration profiles for species, A, I, and P with the condition that $k_2 \ll k_1 = k_{-1}$. When $k_1 = k_{-1}$, we expect $[\mathrm{A}] = [\mathrm{I}]$. As can be seen from the figure, after a short initial startup time, the concentrations of species A and I are approximately equal during the reaction.

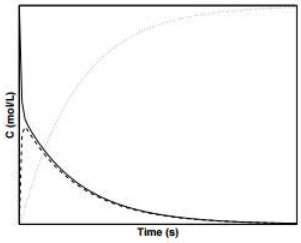


Figure 1.20.4: Plots of [A] (solid line), [I] (dashed line) and [P] (dotted line) over time for $k_2 \ll k_1 = k_{-1}$.

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1.21: Nonlinear kinetics and oscillating reactions

The Complexity of Multi-Step Chemical Reactions

It should be clear by now that chemical kinetics is governed by the mathematics of systems of differential equations. Thus far, we have only looked at reaction systems that give rise to purely *linear* differential equations, however, in many instances the rate equations are nonlinear. When the differential equations are nonlinear, the behavior is considerably more complex. In particular, nonlinear equations can lead to oscillatory solutions and can also exhibit the phenomenon of *chaos*. Chaotic systems are systems that are highly sensitive to small changes in the parameters of the equations or in the initial conditions. Basically, this means that the behavior of a chaotic system can be unpredictable, since such small changes can occur in the form of small errors in determining the parameters (rounding to the nearest tenth or hundredth) or in specifying the initial conditions, and these small changes can cause the system to evolve in time in a very different way.

In order to illustrate the concept of chaos, consider a very typical and well known system, the Lorenz equations. These actually closely resemble the kinds of equations that arise in the study of nonlinear chemical kinetics. In this case, the differential equations are stated for three variables $x(t)$, $y(t)$, and $z(t)$:

$$\frac{dx}{dt} = \sigma(x - y) \tag{1.21.1}$$

$$\frac{dy}{dt} = x(\rho - z) - y \tag{1.21.2}$$

$$\frac{dz}{dt} = xy - \beta z \tag{1.21.3}$$

where σ, ρ, and β are the parameters, and the equations have as initial conditions $x(0) = x_0$, $y(0) = y_0$, and $z(0) = z_0$. These equations cannot be solved analytically, but we can solve them very accurately using a computer program. The trajectory in x, y, and z space can be viewed dynamically on the following Wikipedia page: en.Wikipedia.org/wiki/Lorenz_system. If you follow the trajectory point $\mathbf{r}(t) = (x(t), y(t), z(t))$, you'll see that the motion is highly unpredictable, although it stays on a series of two rings, its motion from one ring to another appears to be random, even though the motion is entirely deterministic.

Keep the Lorenz system in mind as we now explore nonlinear chemical kinetics.

The Iodine Clock Reaction

The iodine clock reaction is a popular chemistry experiment in which one can visualize how different rate constants in consecutive reactions affect the concentration of species during the reaction. Iodine anions (I^-) are colorless. When I^- is reacted with hydrogen peroxide and protons, triiodide is formed, which has a dark blue color. Consider the following series of irreversible reactions:

$$H_2O_2 + 3\,I^- + 2\,H^+ \xrightarrow{k_1} I_3^- + 2\,H_2O \tag{1.21.4}$$

$$I_3^- + 2\,S_2O_3^{2-} \xrightarrow{k_2} 3\,I^- + S_4O_6^{2-} \tag{1.21.5}$$

The rate laws for this system are

$$\frac{d[I_3^-]}{dt} = k_1[I^-]^3 - k_2[I_3^-][S_2O_3^{2-}]^2 \tag{1.21.6}$$

$$\frac{d[I^-]}{dt} = -k_1[I^-]^3 + 3k_2[I_3^-][S_2O_3^{2-}]^2 \tag{1.21.7}$$

$$\frac{d[S_2O_3^{2-}]}{dt} = -k_2[I_3^-][S_2O_3^{2-}]^2 \tag{1.21.8}$$

In order to make the equations look a little simpler, let us introduce the variables:

$$x = [I^-], \quad y = [I_3^-], \quad z = [S_2O_3^{2-}] \tag{1.21.9}$$

In terms of these, the rate equations are

$$\frac{dx}{dt} = -k_1x^3 + 3k_2yz^2 \tag{1.21.10}$$

$$\frac{dy}{dt} = k_1x^3 - k_2yz^2 \tag{1.21.11}$$

$$\frac{dz}{dt} = -k_2yz^2 \tag{1.21.12}$$

If we solve these numerically, we find the following time dependence of the three concentrations: This is a clear example of nonlinearity. Note how the concentration of I_3^- remains close to 0 for a period of time and then suddenly starts to increase. In a sense, think of the "straw that broke the

camel's back". As we pile straws on the back of the camel, the camel remains upright until that last straw, which suddenly breaks the back of the camel, and the camel suddenly falls to the ground. This is also an illustration of nonlinearity.



Video* 1.21.1*: *Famous iodine clock reaction: oxidation of potassium iodide by hydrogen peroxide (https://www.youtube.com/watch?v=_qhYDuJt8fI).*

Despite the complexity of the rate equations, we can still analyze the approximately and predict the behavior seen in Figure 1.21.1. In this reaction mechanism, $k_2 \gg k_1$. Given the rate law for I_3^-,

$$\frac{d[I_3^-]}{dt} = k_1[I^-]^3 - k_2[I_3^-][S_2O_3^{2-}]^2 \tag{1.21.13}$$

if we use the steady-state approximation, we can set the $\frac{d[I_3^-]}{dt}$ equal to 0, yielding

$$[I_3^-] = \frac{k_1}{k_2}\frac{[I^-]^3}{[S_2O_3^{2-}]^2} \tag{1.21.14}$$

Since $k_2 \gg k_1$, the concentration of $[I_3^-]$ is approximately 0 as long as there are $S_2O_3^{2-}$ ions present. As soon as all of the $S_2O_3^{2-}$ is consumed, the concentration of I_3^- can build up in the solution, changing the solution to a dark blue color. Figure 1.21.1 displays the concentration profiles for I^-, I_3^-, and $S_3O_3^{2-}$. As can be seen from the figure, the concentration of I_3^- (red line) remains at approximately $0\ \text{mol/L}$ until all of the $S_2O_3^{2-}$ (blue line) has been depleted.

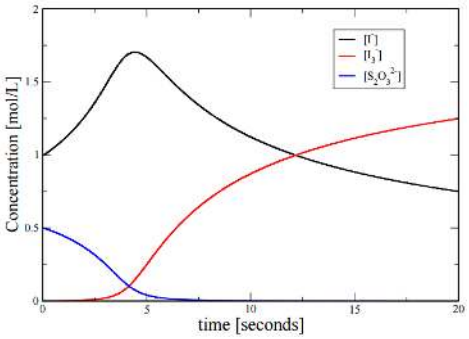


Figure 1.21.1: Concentrations as functions of time of the three species in the iodine clock reaction.

Oscillating Reactions

In all of the examples we have seen thus far, the concentration of intermediate species displays a single maximum during the course of the reaction. There is another class of reactions called *oscillating reactions* in which the concentration of intermediate species oscillates with time. Consider the following series of reactions

$$\mathrm{A} + \mathrm{Y} \xrightarrow{k_1} \mathrm{X} \tag{1.21.15}$$

$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_2} \mathrm{P} \tag{1.21.16}$$

$$\mathrm{B} + \mathrm{X} \xrightarrow{k_3} 2\,\mathrm{X} + \mathrm{Z} \tag{1.21.17}$$

$$2\,\mathrm{X} \xrightarrow{k_4} \mathrm{Q} \tag{1.21.18}$$

$$\mathrm{Z} \xrightarrow{k_5} \mathrm{Y} \tag{1.21.19}$$

In the above reaction mechanism, A and B are reactants; X, Y, and Z are intermediates; and P and Q are products. The third reaction in which B and X react to form X and Z is known as an "autocatalytic reaction" in which at least one of the reactants is also a product. Such reactions are a key feature of oscillating reactions, as will be discussed below.



***Video* 1.21.2:** *The famous Belousov Zhabotinsky chemical reaction in a petri dish. The action is speeded up 8 x from real life. Pacemaker nucleation sites emit circular waves. Breaking the wavefront with a wire triggers pairs of spiral defects which emit more closely spaced waves which eventually fill the container (https://www.youtube.com/watch?v=3JAqrRnKFHo).*

Let us assume that the concentrations of A and B are large, such that we can approximate them to be constant with time. The rate equation for species X can be written as

$$\frac{d\,[\mathrm{X}]}{dt} = k_1\,[\mathrm{A}]\,[\mathrm{Y}] - k_2\,[\mathrm{X}]\,[\mathrm{Y}] + k_3\,[\mathrm{B}]\,[\mathrm{X}] - 2k_4\,[\mathrm{X}]^2 \tag{1.21.20}$$

Using the steady-state approximation, we can set $d\mathrm{X}/dt = 0$ and rewrite Equation 1.21.20 as

$$(-2k_4)\,[\mathrm{X}]^2 + (k_2\,[\mathrm{Y}] - k_3\,[\mathrm{B}])\,[\mathrm{X}] + k_1\,[\mathrm{A}]\,[\mathrm{Y}] = 0 \tag{1.21.21}$$

We can then use the quadratic formula to solve for X:

$$[\mathrm{X}] = -\frac{(k_2\,[\mathrm{Y}] - k_3\,[\mathrm{B}]) \pm \sqrt{(k_2[\mathrm{Y}] - k_3[\mathrm{B}])^2 - 4\,(-2k_4)\,(k_1\,[\mathrm{A}]\,[\mathrm{Y}])}}{2\,(-2k_4)} \tag{1.21.22}$$

Thus, there are two solutions for the concentration of X accessible to the reaction system. To examine solutions for $[\mathrm{X}]$, let us first assume that $[\mathrm{Y}]$ is large. Under these conditions, the first two reactions in the reaction mechanism largely determine the concentration of $[\mathrm{X}]$. We can thus approximate Equation 1.21.20 as

$$0 \approx k_1\,[\mathrm{A}]\,[\mathrm{Y}] - k_2\,[\mathrm{X}]\,[\mathrm{Y}] \tag{1.21.23}$$

Solving for $[\mathrm{X}]$ yields

$$[\mathrm{X}] \approx \frac{k_1\,[\mathrm{A}]}{k_2} \tag{1.21.24}$$

As the reaction continues, species Y is depleted and the assumption that $[\mathrm{Y}]$ is large becomes invalid. Instead the 3^{rd} and 4^{th} steps of the reaction mechanism determine the concentration of X. In this limit, we can approximate Equation 1.21.20 as

$$0 \approx k_3\,[\mathrm{B}]\,[\mathrm{X}] - 2k_4\,[\mathrm{X}]^2 \tag{1.21.25}$$

Solving for $[\mathrm{X}]$ yields

$$[\mathrm{X}] \approx \frac{k_3\,[\mathrm{B}]}{2k_4} \tag{1.21.26}$$

In the second mechanism, the autocatalytic reaction step leads to an increase in the concentration of **X** and **Z**, which in turn leads to an increase in the concentration of **Y**. The feedback loop between the production of species **X** and **Y** leads to oscillatory behavior in the system. This reaction mechanism is known as the Belousov-Zhabotinksii reaction first discovered in the 1950s.

- The autocatalytic reaction of **X** in which **X** reacts with **B** to form more **X** in reaction **3**
- The regeneration of species **Y** in reaction **5**
- The competition between reaction **2** and **3** for the consumption of **X** and the involvement of **Y** in reaction **2**

The actual Belousov-Zhabotinskii reaction is complex, involving many individual steps, and involves the oscillation between the concentration of $HBrO_2$ and Br^-. The reaction equations are

$$BrO_3^- + Br^- + 2\,H^+ \longrightarrow HBrO_2 + HOBr \tag{1.21.27}$$
$$HBrO_2 + Br^- + H^+ \longrightarrow 2\,HOBr \tag{1.21.28}$$
$$HOBr + Br^- + H^+ \longrightarrow Br_2 + H_2O \tag{1.21.29}$$
$$2\,HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \tag{1.21.30}$$
$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2\,BrO_2 + H_2O \tag{1.21.31}$$
$$BrO_2 + Ce^{3+} + H^+ \longrightarrow HBrO_2 + Ce^{4+} \tag{1.21.32}$$
$$BrO_2 + Ce^{4+} + H_2O \longrightarrow BrO_3^- + Ce^{3+} + 2\,H^+ \tag{1.21.33}$$

The essential steps in this mechanism can be reduced to the following set of reactions. Note that we leave this unbalanced and only include the species whose concentrations as functions of time we seek.

$$BrO_3^- + Br^- \xrightarrow{k_1} HBrO_2 + HOBr \tag{1.21.34}$$
$$HBrO_2 + Br^- \xrightarrow{k_2} 2\,HOBr \tag{1.21.35}$$
$$BrO_3^- + HBrO_2 \xrightarrow{k_3} 2\,HBrO_2 + 2\,Ce^{4+} \tag{1.21.36}$$
$$2\,HBrO_2 \xrightarrow{k_4} BrO_3^- + HOBr \tag{1.21.37}$$
$$Ce^{4+} \xrightarrow{k_5} f Br^- \tag{1.21.38}$$

Setting the variables as follows:

$$x = [HBrO_2], \quad y = [Br^-], \quad z = [Ce^{4+}] \tag{1.21.39}$$

We make the approximation that $[BrO_3^-]$ to be a constant a. In this case, the rate equations become

$$\frac{dx}{dt} = k_1 a y - k_2 x y + k_3 a x - k_4 x^2 \tag{1.21.40}$$
$$\frac{dy}{dt} = -k_1 a y - k_2 x y + f k_5 z \tag{1.21.41}$$
$$\frac{dz}{dt} = 2 k_3 a x - k_5 z \tag{1.21.42}$$

Solving these equations numerically, we obtain the trajectory of two of the species show in the Figure **1.21.2**.

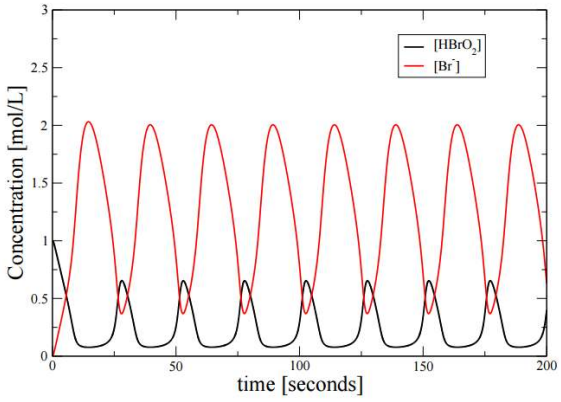


Figure **1.21.2**: Oscillating pattern of the concentrations in the Belousov-Zhabotinskii reaction.

On the other hand, we can drive this system to become chaotic by changing the parameters a little. When this is done, we find the follow plot of the concentration of x:

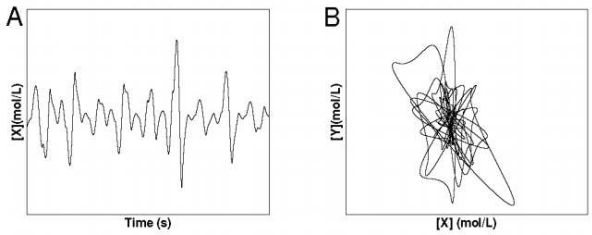


Figure **1.21.3**: Chaotic behavior in the Belousov-Zhabotinskii reaction.

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1.22: Kinetics of Catalysis

As can be seen from the Arrhenius equation, the magnitude of the activation energy, E_a, determines the value of the rate constant, k, at a given temperature and thus the overall reaction rate. Catalysts provide a means of reducing E_a and increasing the reaction rate. Catalysts are defined as substances that participate in a chemical reaction but are not changed or consumed. Instead they provide a new mechanism for a reaction to occur which has a lower activation energy than that of the reaction without the catalyst. *Homogeneous catalysis* refers to reactions in which the catalyst is in solution with at least one of the reactants whereas *heterogeneous catalysis* refers to reactions in which the catalyst is present in a different phase, usually as a solid, than the reactants. Figure 1.22.1 shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

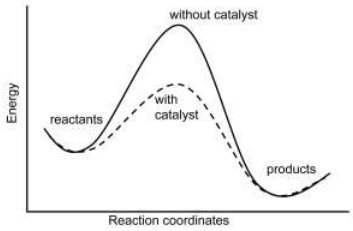


Figure 1.22.1: Comparison of energy profiles with and without catalyst present.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P} \tag{1.22.1}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \tag{1.22.2}$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{\mathrm{cat}}} \mathrm{P} + \mathrm{C} \tag{1.22.3}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{\mathrm{cat}}[\mathrm{A}][\mathrm{C}] \tag{1.22.4}$$

where the first term represents the uncatalyzed reaction and the second term represents the catalyzed reaction. Because the reaction rate of the catalyzed reaction is often magnitudes larger than that of the uncatalyzed reaction (i.e. $k_{\mathrm{cat}} \gg k$), the first term can often be ignored.

Example of Homogenous Catalysis: Acid Catalysis

A common example of homogeneous catalysts are acids and bases. For example, given an overall reaction is $\mathrm{S} \rightarrow \mathrm{P}$. If k is the rate, then

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}] \tag{1.22.5}$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S} + \mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{1.22.6}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{1.22.7}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{1.22.8}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] \tag{1.22.9}$$

$$\frac{d[\mathrm{A}H]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_{-3}[\mathrm{A}H] + k_3[H_3O^+][\mathrm{A}^-] \tag{1.22.10}$$

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{S}H^+] \tag{1.22.11}$$

$$\frac{d[\mathrm{A}^-]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{A}^-][H_3O^+] + k_{-3}[\mathrm{A}H] \tag{1.22.12}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] \tag{1.22.13}$$

$$\frac{d[H_3O^+]}{dt} = -k_2[\mathrm{S}H^+] - k_3[H_3O^+][\mathrm{A}^-] + k_{-3}[\mathrm{A}H] \tag{1.22.14}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}[\mathrm{A}^-]$ and $k_2 \ll k_{-1}[\mathrm{A}^-]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{A}^-][\mathrm{S}H^+] - k_2[\mathrm{S}H^+] = 0 \tag{1.22.15}$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$[\mathrm{S}H^+] = \frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2} \tag{1.22.16}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2} \tag{1.22.17}$$

In the case where $k_2 \gg k_{-1}[\mathrm{A}^-]$, Equation 1.22.17 can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] \tag{1.22.18}$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}[\mathrm{A}^-]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-]} = \frac{k_1k_2}{k_{-1}K}[\mathrm{S}][H^+] \tag{1.22.19}$$

where K is the acid dissociation constant:

$$K = \frac{[\mathrm{A}^-][H^+]}{[\mathrm{A}H]} \tag{1.22.20}$$

In this case, the reaction is hydrogen ion-catalyzed.

Example of Heterogeneous Catalysis: Surface Catalysis of Gas-Phase Reactions

Many gas-phase reactions are catalyzed on a solid surface. For a first-order, unimolecular reaction, the reaction mechanism can be written as

$$\mathrm{A}(g) + \mathrm{S}(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}(s) \tag{1.22.21}$$

$$\mathrm{AS}(s) \xrightarrow{k_2} \mathrm{P}(g) + \mathrm{S}(g) \tag{1.22.22}$$

where the first step is reversible adsorption of the gas molecule, A, onto active sites on the catalyst surface, S, to form a transition state, AS, and the second step is the conversion of adsorbed A molecules to species P. Applying the steady-state approximation to species AS, we can write

$$\frac{d[\mathrm{AS}]}{dt} = k_1[\mathrm{A}][\mathrm{S}] - k_{-1}[\mathrm{AS}]_{ss} - k_2[\mathrm{AS}]_{ss} = 0 \tag{1.22.23}$$

Because the concentration of total active sites on the catalyst surface is fixed at $[\mathrm{S}]_0$, the concentration of adsorbed species on the catalyst surface, $[\mathrm{AS}]$ can be written as

$$[\mathrm{AS}] = \theta\,[\mathrm{S}]_0 \tag{1.22.24}$$

and $[\mathrm{S}]$ can be written as

$$[\mathrm{S}] = (1-\theta)\,[\mathrm{S}]_0 \tag{1.22.25}$$

where θ is the fractional surface coverage of species A on the catalyst surface. We can now write Equation 1.22.23 as

$$k_1\,[\mathrm{A}]\,(1-\theta)\,[\mathrm{S}]_0 - (k_{-1}+k_2)\,\theta\,[\mathrm{S}]_0 = 0 \tag{1.22.26}$$

Rearranging the above equation in terms of θ yields

$$\theta = \frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}] + k_{-1} + k_2} \tag{1.22.27}$$

The rate of production of P can be written as

$$\frac{d\,[\mathrm{P}]}{dt} = k_2\,[\mathrm{AS}]_{ss} = k_2\theta\,[\mathrm{S}]_0 = \frac{k_1 k_2}{k_1\,[\mathrm{A}] + k_{-1} + k_2}\,[\mathrm{A}]\,[\mathrm{S}]_0 \tag{1.22.28}$$

From the above equation, we can observe the importance of having high surface areas for catalytic reactions.

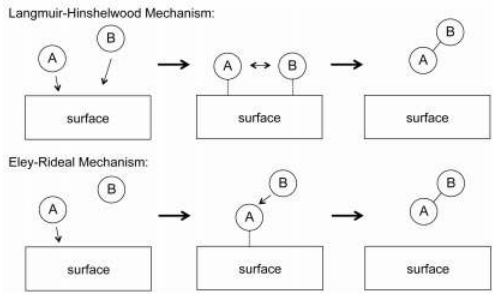


Figure 1.22.2: Illustrations of the Langmuir-Hinshelwood and Eley-Rideal mechanisms for heterogeneous catalysis of bimolecular gas-phase reactions.

For bimolecular gas-phase reactions, two generally-used mechanisms to explain reactions kinetics are the Langmuir-Hinshelwood and Eley-Rideal mechanisms, shown in Figure 1.22.2. In the Langmuir-Hinshelwood mechanism, A and B both adsorb onto the catalyst surface, at which they react to form a product. The reaction mechanism is

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s) \tag{1.22.29}$$

$$\mathrm{B}\,(g) + \mathrm{S}\,(s) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{BS}\,(s) \tag{1.22.30}$$

$$\mathrm{AS}\,(s) + \mathrm{BS}\,(s) \overset{k_3}{\rightarrow} \mathrm{P} \tag{1.22.31}$$

The rate law for the Langmuir-Hinshelwood mechanism can be derived in a similar manner to that for unimolecular catalytic reactions by assuming that the total number of active sites on the catalyst surface is fixed. In the Eley-Rideal mechanism, only one species adsorbs onto the catalyst surface. An example of such a reaction is the partial oxidation of ethylene into ethylene oxide, as shown in Figure 1.22.3. In this reaction, diatomic oxygen adsorbs onto the catalytic surface where it reacts with ethylene molecules in the gas phase.

The reactions for the Eley-Rideal mechanism can be written as

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s) \tag{1.22.32}$$

$$\mathrm{AS}\,(s) + \mathrm{B}\,(g) \overset{k_2}{\rightarrow} \mathrm{P}\,(g) + \mathrm{S}\,(s) \tag{1.22.33}$$

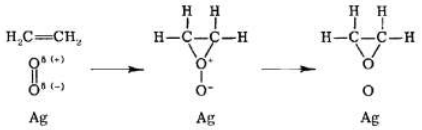


Figure 1.22.3: Illustrations of the reaction mechanism for the partial oxidation of ethylene to ethylene oxide. [Reproduced from Kilty, PA and WMH Sacthler. Catal. Rev., 10, *1]*

Assuming that $k_{-1} \gg k_1$, we can apply a steady-state approximation to species **AS**:

$$\frac{d[\mathrm{AS}]}{dt} = 0 = k_1[\mathrm{A}][\mathrm{S}] - k_{-1}[\mathrm{AS}]_{ss} - k_2[\mathrm{AS}]_{ss}[\mathrm{B}] \tag{1.22.34}$$

As in the case of unimolecular catalyzed reactions, we can express the concentrations of **AS** and **S** in terms of a fraction of the total number of active sites, S_0 and rewrite the above equation as

$$0 = k_1[\mathrm{A}](1-\theta)[\mathrm{S}]_0 - k_{-1}[\mathrm{S}]_0 - k_2\theta[\mathrm{S}]_0[\mathrm{B}] \tag{1.22.35}$$

Solving for θ yields

$$\theta = \frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1} + k_2[\mathrm{B}]} \tag{1.22.36}$$

Furthermore, if $k_2 \ll k_1$ and k_{-1}, we can simplify θ to

$$\theta = \frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1}} \tag{1.22.37}$$

The rate of production of **P** can be expressed as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{AS}]_{ss}[\mathrm{B}] = k_2\theta[\mathrm{S}]_0[\mathrm{B}] = \frac{k_1k_2[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1}}[\mathrm{S}]_0[\mathrm{B}] \tag{1.22.38}$$

We can also write the above expression in terms of the equilibrium constant, K, which is equal tok_1/k_{-1}

$$\frac{d[\mathrm{P}]}{dt} = Kk_2[\mathrm{B}]\frac{K[\mathrm{A}]}{K[\mathrm{A}]+1} \tag{1.22.39}$$

Michaelis-Menten Enzyme Kinetics

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products. In 1913, Leonor Michaelis and Maude Menten proposed the following reaction mechanism for enzymatic reactions:

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \overset{k_2}{\rightarrow} \mathrm{E} + \mathrm{P} \tag{1.22.40}$$

where **E** is the enzyme, **ES** is the enzyme-substrate complex, and **P** is the product. In the first step, the substrate binds to the active site of the enzyme. In the second step, the substrate is converted into the product and released from the substrate. For this mechanism, we can assume that the concentration of the enzyme-substrate complex, \(\text{ES}|), is small and employ a steady-state approximation:

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} - k_2[\mathrm{ES}]_{ss} \approx 0 \tag{1.22.41}$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$[\mathrm{E}]_0 = [\mathrm{ES}] + [\mathrm{E}] \tag{1.22.42}$$

Plugging Equation 1.22.42 into Equation 1.22.41, we obtain

$$0 = k_1([\mathrm{E}]_0 - [\mathrm{ES}]_{ss})[\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} + k_2[\mathrm{ES}]_{ss} \tag{1.22.43}$$

Solving for $[ES]_{ss}$

$$[ES]_{ss} = \frac{k_1 [E]_0 [S]}{k_1 [S] + k_{-1} + k_2} = \frac{[E]_0 [S]}{[S] + \frac{k_{-1} + k_2}{k_1}} \tag{1.22.44}$$

We can then write the reaction rate of the product as

$$\frac{d[P]}{dt} = k_2 [ES]_{ss} = \frac{k_2 [E]_0 [S]}{[S] + \frac{k_{-1} + k_2}{k_1}} = \frac{k_2 [E]_0 [S]}{[S] + K_M} \tag{1.22.45}$$

where K_M is the Michaelis constant. Equation 1.22.45 is known as the Michaelis-Menten equation. The result for Michaelis-Menten kinetics equivalent to that for a unimolecular gas phase reaction catalyzed on a solid surface. In the limit where there is a large amount of substrate present ($[S] \gg K_M$) Equation 1.22.45 reduces to

$$\frac{d[P]}{dt} = r_{max} = k_2 [E]_0 \tag{1.22.46}$$

which is a 0^{th} order reaction, since $[E]_0$ is a constant. The value $k_2 [E]_0$ represents the maximum rate, r_{max}, at which the enzymatic reaction can proceed. The rate constant, k_2, is also known as the *turnover number*, which is the number of substrate molecules converted to product in a given time when all the active sites on the enzyme are occupied. Figure 1.22.4 displays the dependence of the reaction rate on the substrate concentration, [S]. This plot is known as the Michaelis-Menten plot. Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2 [E]_0$ at large values of [S].

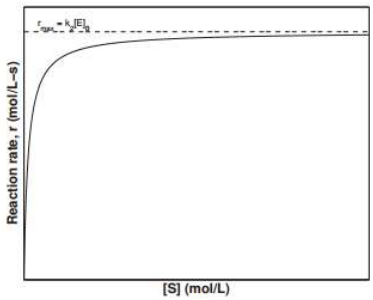


Figure 1.22.4: Rate dependence on substrate concentration for an enzymatic reaction.

Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in with the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/[S]$. Rearranging Equation 1.22.45,

$$\frac{1}{r} = \frac{K_M + [S]}{k_2 [E]_0 [S]} = \frac{K_M}{k_2 [E]_0} \frac{1}{[S]} + \frac{1}{k_2 [E]_0} \tag{1.22.47}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M / k_2 [E]_0$ and y-intercept equal to $1/k_2 [E]_0$.

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1.23: Continuously stirred tank reactors

Thus far in our study of chemical kinetics, we have considered reactions in isothermal batch reactors, in which reactions taking place in closed containers maintained at a constant temperature. While such reactions are commonplace in chemistry labs, most industrial processes instead use continuously stirred tank reactors (CSTRs). In these reactors, reactants are continuously flowed into the reactor, where they undergo a chemical reaction. Simultaneously, an exit stream is extracted from the reactor at the same flow rate as the inlet stream to maintain a constant volume inside the reactor. CSTRs allow for the continuous production of the desired chemical without the need to repeatedly empty and fill the tank. Figure 24.1 displays diagrams for a batch reactor and CSTR. The molar flow rates of species j into and out of the CSTR are denoted by F_{j0} and F_j, respectively, with units of $\mathbf{mol/s}$. Because the contents of the reactors are constantly stirred, we can assume that the contents of the reactor are uniform everywhere.

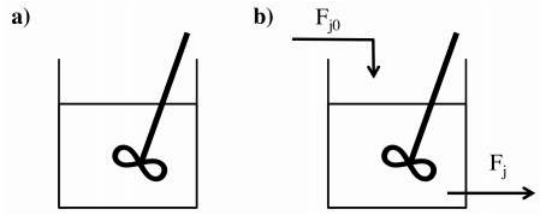


Figure 24.1: Diagrams of a) a batch reactor and b) a CSTR.

Mass Balance for a CSTR

A mass balance on species j in the CSTR can be written as

$$\begin{aligned}&[\text{accumulation of species } j]\\ &= [\text{flow of species } j \text{ in}] - [\text{flow of species } j \text{ out}] + [\text{generation of species } j]\end{aligned} \tag{1.23.1}$$

Formally, we can write the mass balance as:

$$\frac{dN_j}{dt} = F_{j0} - F_j + Vr_j \tag{1.23.2}$$

where N_j is the number of moles of species j, V is the volume of the reactor, with units of $\mathbf{m^3}$, and r_j is the reaction rate of species j, with units of $\mathbf{mol/m^3s}$.

To express the mass balance in terms of concentration, we can use the fact that the molar flow rate of species j is equal to the volumetric flowrate, v, multiplied by the concentration species J:

$$F - j = v\,[j] \tag{1.23.3}$$

Equation 24.1 thus becomes

$$V\frac{d\,[j]}{dt} = v\,([j]_0 - [j])\,Vr_j\nu_j \tag{1.23.4}$$

where v is the volumetric flow rate into and out of the reactor, with units of $\mathbf{m^3/s}$, and ν_j is the stoichiometric coefficient of species j in the reaction. If the rate law is, for example $r_j = \pm\,[j]^{\nu_j}$, then the kinetic equations become

$$V\frac{d\,[j]}{dt} = v\,([j]_0 - [j]) + V\nu_j\,[j]^{\nu_j} \tag{1.23.5}$$

which constitutes a set of nonlinear differential equations. If there are multiple reactants and multiple steps in the reaction, then the kinetic equations are even more complicated. However, note what differs between these kinetic equations and those of a batch reactor is really the flow term $v\,([j]_0 - [j])$.

After an initial time period to start the CSTR, we can assume that the reactor is operating at steady-state, so that $d\,[j]\,/dt = 0$. We can then write Equation 24.3 as:

$$v\,([j]_0 - [j]) + Vr_j = 0 \tag{1.23.6}$$

Dividing the volume, V, by the volumetric flow rate, v, gives a parameter with the units of time, which is defined as τ, or the residence time in the reactor:

$$\tau = \frac{V}{v} \tag{1.23.7}$$

The residence time represents the average amount of time a molecule spends inside the reactor from the time at which it enters the reactor to the time it leaves. Combining Equations 24.5 and 24.6, we arrive at the design equation for CSTRs:

$$[j]_0 - [j] = -\tau r_j \tag{1.23.8}$$

Note that if $[j]_0 - [j] > 0$, then j is depleted in the reaction, and this means that $r_j < 0$, as we would expect if, for example, j is a reactant. On the other hand, if $[j]_0 - [j] < 0$, then j is generated, and $r_j > 0$, as we would expect if, for example, j is a product. The key parameter in the design equation is the residence time τ, which is a design feature.

Fractional Conversion in CSTRs

In batch reactors, the degree of conversion of reactants to products depends on the amount of time the reaction is allowed to proceed. In CSTRs operating at steady-state, on the other hand, the fractional conversion depends on the residence time τ and the volume of the reactor. Consider the following first-order irreversible reaction:

$$\mathrm{A} \longrightarrow \mathrm{B} \tag{1.23.9}$$

with the following rate law:

$$r_\mathrm{A} = -k\,[\mathrm{A}] \tag{1.23.10}$$

We can define the fractional conversion, X, of species A in the CSTR as

$$[\mathrm{A}] = [\mathrm{A}]_0\,(1 - X) \tag{1.23.11}$$

Plugging Equations 24.8 and 24.9 into Equation 24.7 and rearranging, we can write

$$[\mathrm{A}]_0\,X = \tau k\,[\mathrm{A}] = \tau k\,[\mathrm{A}]_0\,(1 - X) \tag{1.23.12}$$

and solve explicitly for the fractional conversion, X,

$$X = \frac{k\tau}{1 + k\tau} \tag{1.23.13}$$

We can also rearrange the equation to solve for the concentration of species A in the exit stream:

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + \tau k} \tag{1.23.14}$$

Examining Equation 24.12, we can see that for large values of τk, the concentration of A in the exit stream will be small. The value of τ, in turn, is determined by the reactor volume and flow rates. These equations thus provide a means of designing a reactor in order to achieve a desired production rate. For example, suppose we continuously flow $10\ \mathrm{mol/s}$ of reactant A into a CSTR at a volumetric flow rate $v = 0.1\ \mathrm{m^3/s}$. At an operation temperature of $500\ \mathrm{K}$, the rate constant, k, for the reaction is measured to be $0.1\ \mathrm{s^{-1}}$. To achieve a fractional conversion of 0.8 such that we produce $8\ \mathrm{mol/s}$ of product B, we can calculate the necessary volume of the reactor using Equations 24.11 and 24.6:

$$X = 0.8 = \frac{0.1\ \mathrm{s^{-1}}\,\tau}{1 + 0.1\ \mathrm{s^{-1}}\,\tau} \tag{1.23.15}$$

Solving for τ,

$$\tau = 40\ \mathrm{s} \tag{1.23.16}$$

Plugging the value of τ into Equation 24.6, we can calculate the reactor volume:

$$V = \tau v = 40\ \mathrm{s} \times 0.1\ \mathrm{m^3/s} = 4\ \mathrm{m^3} = 1057\ \mathrm{gallons} \tag{1.23.17}$$

Similar equations can be derived for more complex reactions simply by using the appropriate rate law in Equation 24.7.

CSTRs in Series

Operating large reactors in industry can be expensive, so a common trick used to reduced costs is to operate multiple CSTRs in series, in which the exit stream of one CSTR is the inlet stream of the next CSTR, as shown in Figure 24.2. Assuming that the

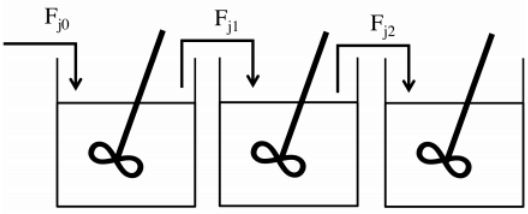


Figure 24.2: Diagram of **3** CSTRs in series.

CSTRs are of equal volume and are operated at the same temperature, the residence time, τ will be the same for each reactor. Consider a first order irreversible reaction of $\mathbf{A} \rightarrow \mathbf{B}$. For the first reactor, the concentration in the exit stream, $[\mathrm{A}]_1$, is defined by

$$[\mathrm{A}]_1 = \frac{[\mathrm{A}]_0}{(1 + k\tau_1)} \tag{1.23.18}$$

The exit stream of reactor **1** then becomes the inlet stream of reactor **2**. We can thus calculate the concentration of the exit stream of reactor **2**, $[\mathrm{A}]_2$ as

$$[\mathrm{A}]_2 = \frac{[\mathrm{A}]_1}{(1 + k\tau_1)} = \frac{[\mathrm{A}]_0}{(1 + k\tau)\,(1 + k\tau)} = \frac{[\mathrm{A}]_0}{(1+k\tau)^2} \tag{1.23.19}$$

For n reactors in series, we can write the general expression:

$$[\mathrm{A}]_n = \frac{[\mathrm{A}]_0}{(1+k\tau)^n} \tag{1.23.20}$$

The fractional conversion parameter becomes

$$X\,(n) = \frac{[\mathrm{A}]_0 - [\mathrm{A}]_n}{[\mathrm{A}]_0} = \frac{(1+k\tau)^n - 1}{(1+k\tau)^n} \tag{1.23.21}$$

As shown in Figure 24.3, as the number of reactors is increased, the total conversion of **A** increases.

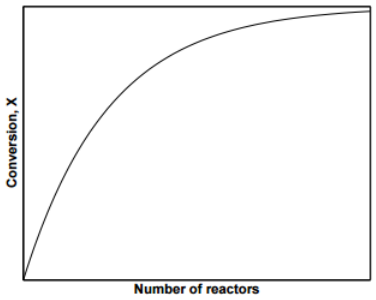


Figure 24.3: Plot of total conversion of species **A** as a function of the number of CSTRs in series.

Energy Balances for Constant-Flow Reactors

A critical parameter of reactor design that has not yet been discussed is the reactor temperature. Because k strongly depends on T, precise control over the reactor temperature is critical in industrial processes. For an open system in which both mass and heat can be exchanged with the surroundings, we can write the energy balance of of the system as

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{DW}{dt} + \sum_j \left(F_j^{(\mathrm{in})} E_j^{(\mathrm{in})} - F_j^{(\mathrm{out})} E_j^{(\mathrm{out})}\right) \tag{1.23.22}$$

where dE/dt is the rate of accumulation of energy in the system, dQ/dt is the rate of heat flow to the system from the surroundings, dW/dt is the rate of work done by the surroundings on the system, $\sum_j F_j^{(\mathrm{in})} E_j^{(\mathrm{in})}$ is the rate of energy added to the system by mass flow into the system, and $\sum_j F_j^{(\mathrm{out})} E_j^{(\mathrm{out})}$ is the rate of energy added to the system by mass flow out the system.

The work term can be expressed as the sum of *shaft work*, W_s, such as that needed to stir the reactor contents, and *flow work* to get mass into and out of the system:

$$\frac{dW}{dt} = \sum_{j=1}^{n} F_j^{(\text{in})} P \nu_j \bar{V}_j^{(\text{in})} - \sum_{j=1}^{n} F_j^{(\text{out})} P \nu_j \bar{V}_j^{(\text{out})} + \frac{dW_s}{dt} \tag{1.23.23}$$

where $\bar{V}_j$ is the specific molar volume of species j. For the purpose of our analysis, we will assume the shaft work to be negligible. the energy balance then becomes

$$\frac{dE}{dt} = \frac{dQ}{dt} + \sum_{j=1}^{n} F_j^{(\text{in})} \left(E_j^{(\text{in})} + P \nu_j \bar{V}_j^{(\text{in})} \right) - \sum_{j=1}^{n} F_j^{(\text{out})} \left(E_j^{(\text{out})} + P \nu_j \bar{V}_j^{(\text{out})} \right) \tag{1.23.24}$$

$$= \frac{dQ}{dt} + \sum_{j=1}^{n} F_j^{(\text{in})} \nu_j \bar{H}_j^{(\text{in})} - \sum_{j=1}^{n} F_j^{(\text{out})} \nu_j \bar{H}_j^{(\text{out})} \tag{1.23.25}$$

We can also express the energy balance in terms of the enthalpy of reaction, $\Delta_r H$. Consider the reaction $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$. We can write the exit flow rates for each species in terms of the inlet flow rates and conversion of A:

$$F_\mathrm{A} = F_{\mathrm{A}0} - F_{\mathrm{A}0} X \tag{1.23.26}$$

$$F_\mathrm{B} = F_{\mathrm{B}0} - F_{\mathrm{A}0} X \tag{1.23.27}$$

$$F_\mathrm{C} = F_{\mathrm{C}0} + F_{\mathrm{A}0} X \tag{1.23.28}$$

$$F_\mathrm{D} = F_{\mathrm{D}0} + F_{\mathrm{A}0} X \tag{1.23.29}$$

Plugging these expressions into Equation 24.21 and rearranging yields

$$\frac{dE}{dt} = \frac{dQ}{dt} + \sum_{j=1}^{n} F_j^{(\text{in})} \nu_j \left(\bar{H}_j^{(\text{in})} - \bar{H}_j^{(\text{out})} \right) - \Delta_r H\left(T\right) F_\mathrm{A}^{(\text{in})} X \tag{1.23.30}$$

where

$$\Delta_r H\left(T\right) = d\bar{H}_\mathrm{D}^{(\text{out})} + c\bar{H}_\mathrm{C}^{(\text{out})} - b\bar{H}_\mathrm{B}^{(\text{out})} - a\bar{H}_\mathrm{A}^{(\text{out})} \tag{1.23.31}$$

Using the relationship $\Delta H = C_P \Delta T$, we can write

$$\frac{dE}{dt} = \frac{dQ}{dt} + \sum_{j=1}^{n} F_j^{(\text{in})} \left(C_{P,j}\right) \left(T_0 - T\right) - \Delta_r H\left(T\right) F_\mathrm{A}^{(\text{in})} X \tag{1.23.32}$$

In the steady state, we can take $dE/dt = 0$, and if the reactions are carried out adiabatically, which requires slow stirring and a low flow rate, then $dQ/dt = 0$ as well. In this case, we can solve for the operational temperature T, which gives

$$T = T_0 - \frac{F_\mathrm{A}^{(\text{in})} X \Delta_r H\left(T\right)}{\Sigma_j F_j^{(\text{in})} C_{P,j}} \tag{1.23.33}$$

In principle, this would need to be solved iteratively, given the temperature dependence of $\Delta_r H\left(T\right)$ on T. However, if we assume that the reaction enthalpy is temperature independent (and that $C_{P,j}$ is also independent of T), then Equation 24.29 gives the temperature directly.

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1.24: Plug flow reactors and comparison to continuously stirred tank reactors

Example 1.24.1: Adiabatic CSTRs

Consider the following first-order irreversible reaction taking place in an adiabatic CSTR:

$$\mathrm{A} \xrightarrow{k} \mathrm{B} + \mathrm{C} \tag{1.24.1}$$

Pure A is fed into the CSTR at a volumetric flow rate of $10\ \mathrm{m^3/s}$ and a temperature, $T_0 = 350\ \mathrm{K}$. The volume of the reactor is $100\ \mathrm{m^3}$. What is the steady-state conversion, X, and temperature, T? Additional information: $C_{p,\mathrm{A}} = 3\ \mathrm{J/mol \cdot K}$, $C_{p,\mathrm{B}} = 2\ \mathrm{J/mol \cdot K}$, $C_{p,\mathrm{C}} = 2\ \mathrm{J/mol \cdot K}$. $\Delta H_{\mathrm{rxn}}\,(350\ \mathrm{K}) = -1500\ \mathrm{J/mol}$, $E_a = 40{,}000\ \mathrm{J/mol}$, $k = 1 \times 10^{-3}\ \mathrm{s^{-1}}$ at $T = 350\ \mathrm{K}$.

Solution

The design equation for a first-order irreversible reaction is given by

$$X = \frac{k\tau}{1 + k\tau} \tag{1.24.2}$$

where

$$k\,(T) = k\,(350\ \mathrm{K})\, e^{-E_a\left(\frac{1}{RT} - \frac{1}{350\ \mathrm{K}}\right)} \tag{1.24.3}$$

Combining the above expressions yields

$$X = \frac{k\,(350\ \mathrm{K})\, e^{-E_a\left(\frac{1}{RT} - \frac{1}{350\ \mathrm{K}}\right)}}{1 + k\,(350\ \mathrm{K})\, e^{-E_a\left(\frac{1}{RT} - \frac{1}{350\ \mathrm{K}}\right)}} \tag{1.24.4}$$

The energy balance for the CSTR can be written as

$$0 = F_{\mathrm{A0}} C_{p,\mathrm{A}}\,(T_0 - T) - \left[\Delta H_{\mathrm{rxn}}\,(350\ \mathrm{K}) + \Delta C_p\,(T - 350\ \mathrm{K})\right] F_{\mathrm{A0}} X \tag{1.24.5}$$

where $\Delta C_p = C_{p,\mathrm{C}} + C_{p,\mathrm{B}} - C_{p,\mathrm{A}}$. Rearranging in terms of X yields

$$X = \frac{C_{p,\mathrm{A}}\,(T_0 - T)}{\Delta H_{\mathrm{rxn}}\,(350\ \mathrm{K}) + \Delta C_p\,(T - 350\ \mathrm{K})} \tag{1.24.6}$$

Equations 1.24.4 and 1.24.6 can be solved simultaneously for X and T. Figure 25.1 displays plots of X versus T from Equation 25.4 (solid line) and Equation 1.24.6 (dashed line). As can be seen from the figure, there are three combinations of X and T that will satisfy the two equations, indicating that there are multiple steady-states at which the reactor can operate.

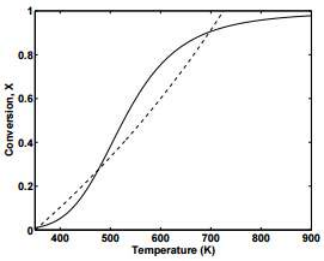


Figure 25.1: Conversion as a function of temperature calculated from the mass balance (solid line) and the energy balance (dashed line).

Plug Flow Reactors (PFRs)

Another type of reactor used in industrial processes is the plug flow reactor (PFR). Like the CSTRs, a constant flow of reactants and products and exit the reactor. In PFRs, however, the reactor contents are not continuously stirred. Instead, chemical species are flowed along a tube as a plug, as shown in Figure 25.2. As the plug of fluid flows through the PFR, reactants are converted into products. In the diagram, $F_{j0} = F_j^{(\mathrm{in})}$, and $F_j = F_j^{(\mathrm{out})}$.

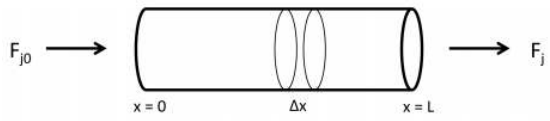


Figure 25.2: Diagram of a PFR.

PFRs are characterized by their length, L, cross-sectional area, A, and linear flow rate of fluids through the reactor, u. For the purpose of our analysis, we will assume PFRs to be cylindrical, that there are no radial variations in the velocity, concentration, temperature or reaction rate along the reactor, and that there is no pressure drop or density variation along the reactor. Based on these assumptions, we can define the linear flow rate of fluid, u, through the tube as

$$u = \frac{v}{A} \tag{1.24.7}$$

where v is the volumetric flow rate and A is the cross-sectional area of the tube. The molar flow rate of species j along the reactor length can be defined in terms of u as

$$F_j(x,t) = v[j](x,t) = uA[j](x,t) \tag{1.24.8}$$

where $[j]$ is a function of x and t. Note that $F_j(x,t)$ satisfies the boundary conditions:

$$F_j(0,t) = F_j^{(\text{in})} \tag{1.24.9}$$

$$F_j(L,t) = F_j^{(\text{out})} \tag{1.24.10}$$

Mass balance for a PFR

As in the case of CSTRs, we can write a mass balance on species j in the PFR as

$$\begin{gathered}[\text{accumulation of species } j] \\ = [\text{flow of species } j \text{ in}] - [\text{flow of species } j \text{ out}] + [\text{generation of species } j]\end{gathered} \tag{1.24.11}$$

Because the concentration of species j varies along the length of the PFR, let us first consider a section of the PFR, Δx. If Δx is sufficiently small, we can make the approximation that the reaction rate, r, is constant within Δx. We can the write the mass balance as

$$\frac{dN_j}{dt} = F_j(x,t) - F_j(x+\Delta x,t) + V\nu_j r_j \tag{1.24.12}$$

where $F_j(x,t)$ is the flow rate *into* the small volume, and $F_j(x+\Delta x,t)$ is the flow rate *out of* the small volume. Since $F_j(x,t) = uA[j](x,t)$ and $F_j(x+\Delta x,t) = uA[j](x+\Delta x,t)$, we can write the mass balance condition as

$$\frac{dN_j}{dt} = V\frac{\partial[j]}{\partial t} = A\Delta x\frac{\partial[j]}{\partial t} = -Au([j](x+\Delta x,t) - [j](x,t)) + A\Delta x\nu_j r_j \tag{1.24.13}$$

Now, we divide by $A\Delta x$, which yields

$$\frac{\partial[j]}{\partial t} = -u\left(\frac{[j](x+\Delta x,t) - [j](x,t)}{\Delta x}\right) + \nu_j r_j \tag{1.24.14}$$

and if we take the limit $\Delta x \to 0$, then the first term on the right becomes a spatial derivative, so that

$$\frac{\partial[j]}{\partial t} + u\frac{\partial[j]}{\partial x} = \nu_j r_j \tag{1.24.15}$$

This constitutes a set of possibly coupled, nonlinear partial differential equations for all species in the reaction. The complexity of the equations is determined by the rate laws r_j for each species. If the rate laws are nonlinear, e.g., $r_j = \pm k[j]^{\nu_j}$ or involve multiple species, as occurs in complex reaction mechanisms, then the equations become rather complicated and need to be solved numerically.

However, let us suppose we can use a steady-state approximation so that $\partial[j]/\partial t = 0$. Then the equation becomes

$$\frac{d[j]}{dx} = \frac{\nu_j}{u} r_j \tag{1.24.16}$$

Examining Equation 25.14, we can see that the extent of conversion of reactants will depend on the length of the reactor, the linear flow rate, u, and the reaction rate.

Fractional conversion in PFRs

For a first-order irreversible reaction in which $\mathbf{A} \rightarrow \mathbf{B}$, the rate law is

$$r_{\mathrm{A}} = -k\,[\mathrm{A}] \tag{1.24.17}$$

and we can write Equation 25.14 as

$$\frac{d\,[\mathrm{A}]}{dx} = -\frac{1}{u}k\,[\mathrm{A}] \tag{1.24.18}$$

Rearranging the above equation,

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d\,[\mathrm{A}]}{[\mathrm{A}]} = -\frac{k}{u}\int_0^x dx' \tag{1.24.19}$$

and integrating

$$\ln \frac{[\mathrm{A}]_x}{[\mathrm{A}]_0} = -\frac{kx}{u} \tag{1.24.20}$$

we can write the dependence of the concentration, $[\mathrm{A}]$, along x as

$$[\mathrm{A}]_x = [\mathrm{A}]_0\, e^{-\frac{kx}{u}} \tag{1.24.21}$$

and the final concentration, $[\mathrm{A}]_L$ as

$$[\mathrm{A}]_L = [\mathrm{A}]_0\, e^{-\frac{kL}{u}} \tag{1.24.22}$$

Recognizing that $\frac{L}{u}$ is equal to the residence time, τ, for PFRs, we can also write the above equation as

$$[\mathrm{A}]_L = [\mathrm{A}]_0\, e^{-k\tau} \tag{1.24.23}$$

Plugging in

$$[\mathrm{A}]_L = [\mathrm{A}]_0\,(1 - X) \tag{1.24.24}$$

we can also write the equation in terms of the fractional conversion

$$X = 1 - e^{-k\tau} \tag{1.24.25}$$

Figure 25.3 displays the concentration profile of species $\mathbf{A}$ along the length of the reactor. As can be seen from the figure, the concentration profile of species $\mathbf{A}$ in a PFR is identical to that in a batch reactor, with the exception that the x-axis is the length of the reactor instead of time. In fact, a PFR is a batch reactor in which we switch from a stationary coordinate system as a function of time to a moving coordinate system as function of distance, such that $dt \rightarrow dx/u$. Thus,

$$\frac{d\,[\mathrm{A}]}{dt} \rightarrow u\frac{d\,[\mathrm{A}]}{dx} = -r\,([\mathrm{A}]) \tag{1.24.26}$$

Now consider a second-order reaction $2\,\mathbf{A} \rightarrow \mathbf{B}$. The rate law is

$$r_{\mathrm{A}} = -k\,[\mathrm{A}]^2 \tag{1.24.27}$$

Thus, the design equation gives the spatial profile of $\mathbf{A}$ as

$$\frac{d\,[\mathrm{A}]}{dx} = -\frac{2k}{u}[\mathrm{A}]^2 \tag{1.24.28}$$

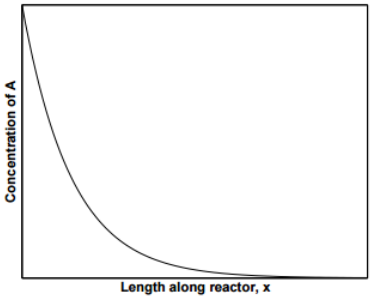


Figure 25.3: Concentration profile of species **A** along the length of a PFR for a first-order irreversible reaction.

This can be solved in the same way that we solve the second-order rate kinetics.

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -\frac{2k}{u}dx \tag{1.24.29}$$

$$-\frac{1}{[\mathrm{A}]} = -\frac{2kx}{u} - C \tag{1.24.30}$$

$$\frac{1}{[\mathrm{A}]} = \frac{2kx}{u} + C \tag{1.24.31}$$

$$[\mathrm{A}](x) = \frac{1}{\frac{2kx}{u} + C} \tag{1.24.32}$$

$$[\mathrm{A}](0) = [\mathrm{A}]_0 = \frac{1}{C} \tag{1.24.33}$$

$$C = \frac{1}{[\mathrm{A}]_0} \tag{1.24.34}$$

$$[\mathrm{A}](x) = \frac{[\mathrm{A}]_0}{1 + \frac{2kx}{u}[\mathrm{A}]_0} \tag{1.24.35}$$

Thus, at the exit stream

$$[\mathrm{A}](L) = \frac{[\mathrm{A}]_0}{1 + \frac{2kL}{u}[\mathrm{A}]_0} = [\mathrm{A}]_0(1 - X) \tag{1.24.36}$$

This gives the conversion fraction as

$$X = \frac{2k\tau[\mathrm{A}]_0}{1 + 2k\tau[\mathrm{A}]_0} \tag{1.24.37}$$

where $\tau = L/u$ is the residence time.

Comparison of CSTRs and PFRs

For a first-order irreversible reaction, recall that the residence time, τ, for a CSTR is

$$\tau_{\mathrm{CSTR}} = \frac{V_{\mathrm{CSTR}}}{v} = \frac{[\mathrm{A}]_0 - [\mathrm{A}]}{k[\mathrm{A}]} \tag{1.24.38}$$

while for a PFR, we can rearrange Equation 25.21 in terms of τ:

$$\tau_{\mathrm{PFR}} = \frac{L_{\mathrm{PFR}}}{u} = \frac{V_{\mathrm{PFR}}}{v} = \frac{1}{k}\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]} \tag{1.24.39}$$

For equal volumetric flowrates into and out of the reactors, the ratio of the residence times of CSTRs and PFRs is equal to the ratio of the volumes of the reactors

$$\frac{\tau_{\mathrm{CSTR}}}{\tau_{\mathrm{PFR}}} = \frac{V_{\mathrm{CSTR}}}{V_{\mathrm{PFR}}} = \frac{[\mathrm{A}]_0 - [\mathrm{A}]}{[\mathrm{A}]\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right)} = \frac{X}{(1-X)\ln\left(\frac{1}{1-X}\right)} \tag{1.24.40}$$

Figure 25.4 displays the plot of $V_{\mathrm{CSTR}}/V_{\mathrm{PFR}}$ as a function of the fractional conversion, X. As can be seen from the figure, the ratio is always positive, indicating that to achieve the same fractional conversion, the volume of a CSTR must be larger than the volume of

a PFR. At high fractional conversion values, the volume required for a CSTR increases rapidly compared the the volume of a PFR. If reactor volume is the only criterion for deciding the type of reactor to use, clearly PFRs are the optimal choice. However, when one considers material costs and ease of operation, CSTRs may still be preferred for some applications.

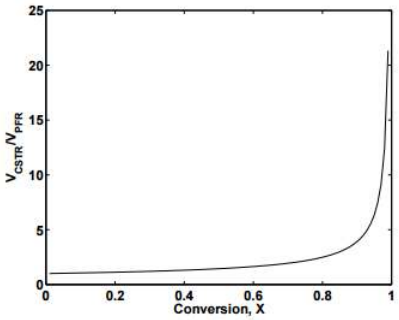


Figure 25.4: Ratio of the volume of a CSTR to a the volume of a PFR as a function of fractional conversion for a first-order irreversible reaction.

Despite Figure 25.4, there are other solutions to this problem. Consider a comparison of a PFR to n CSTRs in series. Recall that the conversion factor as a function of n for CSTRs in series is

$$X(n) = \frac{(1+k\tau)^n - 1}{(1+k\tau)^n} \tag{1.24.41}$$

or

$$1 = (1 + k\tau)(1 - X(n)) \tag{1.24.42}$$

$$(1 + k\tau) = \left[\frac{1}{1-X(n)}\right]^{1/n} \tag{1.24.43}$$

$$k\tau = \frac{1}{(1-X(n))^{1/n}} - 1 \tag{1.24.44}$$

$$\tau = \frac{1}{k}\left[\frac{1-(1-X)^{1/n}}{(1-X)^{1/n}}\right] \tag{1.24.45}$$

This gives

$$\frac{\tau_{\text{CSTR, series}}}{\tau_{\text{PFR}}} = \frac{V_{\text{CSTR, series}}}{V_{\text{PFR}}} = \frac{1-(1-X)^{1/n}}{(1-X)^{1/n}\ \ln(1/(1-X))} \tag{1.24.46}$$

If we now plot this ratio for different values of n, we obtain the figure below:

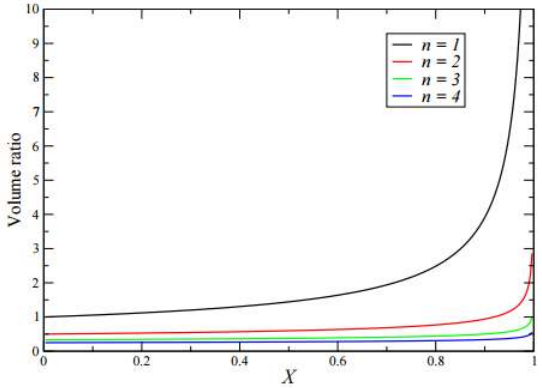


Figure 25.5: Ratio of the volume of a CSTR to a the volume of a PFR as a function of fractional conversion for a first-order irreversible reaction with CSTRs in series.

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