CHM 312: PHYSICAL CHEMISTRY II

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CHM 312: Physical Chemistry II (Lebanon Valley College)

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CHAPTER OVERVIEW

1: Gases and Equations of State

1.1: The Average Translational Kinetic Energy of a Gas

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

One key property of the individual particles is their velocity. However, in a sample of many gas particles, the particles will likely have various velocities. Rather than list the velocity of each individual gas molecule, we can combine these individual velocities in several ways to obtain "collective" velocities that describe the sample as a whole.

Table 27.1.1: Kinetic Properties of a Thermalized Ensemble (i.e., follows Maxwell-Boltzmann Distribution)

Property	Speed	Kinetic Energy
Most probable	$\sqrt{\frac{2k_bT}{m}}$	k_BT
Average	$\sqrt{\frac{8k_bT}{\pi m}}$	$\frac{4k_BT}{\pi}$
Root-mean-square	$\sqrt{\frac{3k_bT}{m}}$	$\frac{3}{2}k_BT$

In the following example, these three collective velocities are defined and calculated for a sample of gas consisting of only eight molecules.

✓ Example 27.1.1 : A Gas Sample with Few Molecules

The speeds of eight molecules were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{avg}) root mean square speed (v_{rms}), and most probable speed (v_{mp}).

Solution

Start with definitions:

- **average speed** (v_{avg}) = the sum of all the speeds divided by the number of molecules
- **root-mean square speed** (v_{rms}) = the square root of the sum of the squared speeds divided by the number of molecules
- **most probable speed** (v_{mp}) = the speed at which the greatest number of molecules is moving

The average speed:

$$\begin{aligned} v_{\text{avg}} &= \frac{(1.0+4.0+4.0+6.0+6.0+6.0+8.0+10.0)\ \text{m/s}}{8} \\ &= 5.6\ m/s \end{aligned}$$

The root-mean square speed:

$$\begin{aligned} v_{\text{rms}} &= \sqrt{\frac{(1.0^2+4.0^2+4.0^2+6.0^2+6.0^2+6.0^2+8.0^2+10.0^2)\ \text{m}^2/\text{s}^2}{8}} \\ &= 6.2\ m/s \end{aligned}$$

The most probable speed:

Of the eight molecules, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three molecules have different speeds. Hence

$$v_{\text{mp}} = 6.0\ m/s.$$

Using expressions for v_{mp}, v_{ave}, or v_{rms} , it is fairly simple to derive expressions for kinetic energy from the expression

$$E_{kin} = \frac{1}{2} m v^2$$

It is important to remember that there will be a full distribution of molecular speeds in a thermalized sample of gas. Some molecules will be traveling faster and some more slowly. It is also important to recognize that the most probable, average, and RMS kinetic energy terms that can be derived from the kinetic molecular theory do not depend on the mass of the molecules (Table 27.1.1). As such, it can be concluded that the average kinetic energy of the molecules in a thermalized sample of gas depends only on the temperature. However, the average speed depends on the molecular mass. So, for a given temperature, light molecules will travel faster on average than heavier molecules.

The calculations carried out in Example 27.1.1 become cumbersome as the number of molecules in the sample of gas increases. Thus, a more efficient way to determine the various collective velocities for a gas sample containing a large number of molecules is required.

1.1.1: A Molecular Description of Pressure and Molecular Speed

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Scotsman James Clerk Maxwell (1831–1879), this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

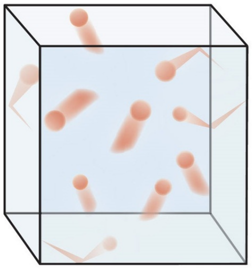

Figure 27.1.1 : Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In Topic 1C, we explain how this theory must be modified to account for the behavior of real gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 27.1.2).

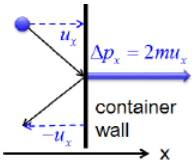

Figure 27.1.2 : Note: In this figure, the symbol u is used to represent velocity. In the rest of this text, velocity will be represented with the symbol v. Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. Momentum transfer ($\Delta\rho_x$) for an elastic collision is equal to mΔv_x, where m is the mass of the molecule and Δv_x is the change in the x component of the molecular velocity ($v_{x_{final}} - v_{x_{initial}}$) .The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction, and Δv_x equals $2v_x$.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity v_x in the x direction hits is expressed as:

$$\text{momentum transfer}_{\text{x}} = \Delta\rho_{\text{x}} = \text{m}\Delta\text{v}_{\text{x}} = 2\text{mv}_{\text{x}} \tag{1.1.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (v_x) \times \left(\frac{N}{V}\right) \tag{1.1.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mv_x) \times (v_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mv_x^2 \tag{1.1.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace v_x^2 in the expression above with the average value of v_x^2, which is denoted by $\overline{v_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{v_x^2} \tag{1.1.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$. Here the quantity $\overline{v^2}$ is called the **mean-square speed** defined as the average value of square-speed (v^2) over all molecules. Since $v^2 = v_x^2 + v_y^2 + v_z^2$ for each molecule, $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$. By substituting $\frac{1}{3}\overline{v^2}$ for $\overline{v_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{v^2} \tag{1.1.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas,

$$\epsilon = m\overline{v^2}/2 \tag{1.1.6}$$

By rearranging equation 1.1.5 and substituting in equation 1.1.6, we obtain

$$PV = \frac{1}{3}Nm\overline{v^2} = \frac{2}{3}N\epsilon \tag{1.1.7}$$

The 2/3 factor in the proportionality reflects the fact that velocity components in each of the three directions contributes ½ *kT* to the kinetic energy of the particle. The average translational kinetic energy is directly proportional to temperature:

$$\epsilon = \frac{3}{2}kT \tag{1.1.8}$$

in which the proportionality constant k is known as the *Boltzmann constant*. Substituting Equation 1.1.8 into Equation 1.1.7 yields

$$PV = \left(\frac{2}{3}N\right)\left(\frac{3}{2}kT\right) = NkT \tag{1.1.9}$$

The Boltzmann constant k is just the gas constant per molecule, so if N is chosen as Avogadro's number, N_A, then $N_A k$ is R, the gas constant per mole. Thus, for *n* moles of particles, the Equation 1.1.9 becomes

$$PV = nRT \tag{1.1.10}$$

which is the ideal gas law.

As noted in Example 27.1.1 , the root-mean square speed (v_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots v_N^2}{N}} \tag{1.1.11}$$

where N is the number of particles and v_i is the speed of particle i.

The v_{rms} for a sample containing a large number of molecules can be obtained by combining equations 1.1.7 and 1.1.8 in a slightly different fashion than that used to obtain equation 1.1.10:

$$PV = \frac{1}{3}Nm\bar{v}^2 = \frac{2}{3}N\epsilon \tag{27.1.10}$$

$$\epsilon = \frac{3}{2}kT \tag{27.1.11}$$

$$\frac{1}{3}Nm\bar{v}^2 = \left(\frac{2}{3}\right)\left(\frac{3}{2}\right)NkT \tag{1.1.12}$$

$$\frac{1}{3}Nm\bar{v}^2 = NkT \tag{1.1.13}$$

$$Nm\bar{v}^2 = 3NkT \tag{1.1.14}$$

If N is chosen to be Avogadro's number, N_A, then $N_A m = M$, the molar mass, and $N_A k = R$, the gas constant per mole,

$$\bar{v}^2 = \frac{3RT}{M} \tag{1.1.15}$$

$$v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}} \tag{1.1.16}$$

In Equation 1.1.16, v_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 1.1.16 shows that v_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

Example 27.1.2 :

What is the root mean-square speed for O_2 molecules at 25ºC?

Given: Temperature in ºC, type of molecules, ideal gas gas constant

Asked for: v_{rms}, the root mean-square speed

Strategy:

Convert temperature to kelvins:

$$\text{T (in kelvin)} = (25^{\text{o}}\text{C} + 273^{\text{o}}\text{C})\frac{1\text{ K}}{1\ ^{\text{o}}\text{C}} = 298\text{ K}$$

Convert molar mass of O_2 molecules to kg per mole:

$$\text{M (in }\frac{\text{kg}}{\text{mole}}) = 32.00\frac{\text{g}}{\text{mole}}\text{x}\frac{1\text{ kg}}{1000\text{ g}} = 0.03200\frac{\text{kg}}{\text{mole}}$$

Use equation 1.1.16to calculate the rms speed.

Solution

$$v_{\text{rms}_{\text{O}_2}} = \sqrt{\frac{3(8.3145\frac{\text{J}}{\text{K}\cdot\text{mole}})(298.15\text{ K})}{0.03200\frac{\text{kg}}{\text{mole}}}} = 482\frac{m}{s}$$

? Exercise 27.1.2

What is the root mean-square speed for Cl_2 molecules at 25ºC?

$$v_{\text{rms}_{\text{Cl}_2}} = 324\frac{m}{s}$$

1.1.2: Many molecules, many velocities

At temperatures above absolute zero, all molecules are in motion. In the case of a gas, this motion consists of straight-line jumps whose lengths are quite great compared to the dimensions of the molecule. Although we can never predict the velocity of a particular *individual* molecule, the fact that we are usually dealing with a huge number of them allows us to know what fraction of the molecules have kinetic energies (and hence velocities) that lie within any given range.

The trajectory of an individual gas molecule consists of a series of straight-line paths interrupted by collisions. What happens when two molecules collide depends on their relative kinetic energies; in general, a faster or heavier molecule will impart some of its kinetic energy to a slower or lighter one. Two molecules having identical masses and moving in opposite directions at the same speed will momentarily remain motionless after their collision.

If we could measure the instantaneous velocities of all the molecules in a sample of a gas at some fixed temperature, we would obtain a wide range of values. A few would be zero, and a few would be very high velocities, but the majority would fall into a more or less well-defined range. We might be tempted to define an average velocity for a collection of molecules, but here we would need to be careful: molecules moving in opposite directions have velocities of opposite signs. Because the molecules are in a gas are in random thermal motion, there will be just about as many molecules moving in one direction as in the opposite direction, so the velocity vectors of opposite signs would all cancel and the average velocity would come out to zero. Since this answer is not very useful, we need to do our averaging in a slightly different way.

The proper treatment is to average the *squares* of the velocities, and then take the square root of this value to obtain the root-mean-square velocity (v_{rms}), which is what we developed above. This velocity describes the gas sample as a whole, but it does not tell us about the range of velocities possible, nor does it tell us the distribution of velocities. To obtain a more complete description of how many gas molecules are likely to be traveling at a given velocity range we need to make use of the Maxwell-Boltzmann distribution law.

Contributors and Attributions

- Mark Tuckerman (New York University)
- Tom Neils, Grand Rapids Community College (editing)

1.2: The Gaussian Distribution of One Component of the Molecular Velocity

As was shown in section 27.1, the pressure of an ideal gas is given as the total force exerted per unit area

$$P = \frac{F_{tot}}{A} = N_{tot}\left(\frac{mv_x^2}{V}\right) = \frac{N_{tot}m}{V}v_x^2$$

The question then becomes how to deal with the velocity term. Initially, it was assumed that all of the molecules had the same velocity, and so the magnitude of the velocity in the x-direction was merely a function of the trajectory. However, real samples of gases comprise molecules with an entire distribution of molecular speeds and trajectories. To deal with this distribution of values, we replaced (v_x^2) with the squared average of velocity in the x direction $\langle v_x \rangle^2$.

$$P = \frac{N_{tot}m}{V}\langle v_x \rangle^2$$

The distribution function for velocities in the x direction, known as the **Maxwell-Boltzmann distribution**, is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}} \tag{1.2.1}$$

This function has two parts: a **normalization constant** and an exponential term. The normalization constant is derived by noting that

$$\int_{-\infty}^{\infty} f(v_x)dv_x = 1 \tag{1.2.2}$$

Normalizing the Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution has to be normalized because it is a continuous probability distribution. As such, the sum of the probabilities for all possible values of v_x **must** be unity. And since v_x can take any value between -∞ and ∞, then Equation 1.2.2 must be true. So if the form of $f(v_x)$ is assumed to be

$$f(v_x) = N\exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

The normalization constant N can be found from

$$\int_{-\infty}^{\infty} f(v_x)dv_x = \int_{-\infty}^{\infty} N\exp\left(\frac{-mv_x^2}{2k_B T}\right)dv_x = 1$$

The expression can be simplified by letting $\alpha = m/2k_B T$:

$$N\int_{-\infty}^{\infty} \exp(-\alpha v_x^2)dv_x = 1$$

A table of definite integrals says that

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

So

$$N\sqrt{\frac{\pi}{\alpha}} = 1$$

Thus,

$$N = \sqrt{\frac{\alpha}{\pi}} = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

And thus the normalized distribution function is given by

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_BT}\right) \tag{1.2.3}$$

Calculating an Average from a Probability Distribution

Calculating an average for a finite set of data is fairly easy. The average is calculated by

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$$

But how does one proceed when the set of data is infinite? Or how does one proceed when all one knows are the probabilities for each possible measured outcome? It turns out that that is fairly simple too!

$$\bar{x} = \sum_{i=1}^{N} x_i P_i$$

where P_i is the probability of measuring the value x_i. This can also be extended to problems where the measurable properties are not discrete (like the numbers that result from rolling a pair of dice) but rather come from a continuous parent population. In this case, if the probability is of measuring a specific outcome, the average value can then be determined by

$$\bar{x} = \int x P(x) dx$$

where $P(x)$ is the function describing the probability distribution, and with the integration taking place across all possible values that x can take.

Calculating the average velocity in the x direction

A value that is useful (and will be used in further developments) is the average velocity in the x direction. This can be derived using the probability distribution, as shown in the mathematical development box above. The average value of v_x is given by

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dx$$

This integral will, by necessity, be zero. This must be the case as the distribution is symmetric, so that half of the molecules are traveling in the +x direction, and half in the –x direction. These motions will have to cancel. So, a more satisfying result will be given by considering the magnitude of v_x, which gives the speed in the x direction. Since this cannot be negative, and given the symmetry of the distribution, the problem becomes

$$\langle |v_x| \rangle = 2\int_{0}^{\infty} v_x f(v_x) dx$$

In other words, we will consider only half of the distribution, and then double the result to account for the half we ignored.

For simplicity, we will write the distribution function as

$$f(v_x) = N \exp(-\alpha v_x^2)$$

where

$$N = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

and

$$\alpha = \frac{m}{2k_BT}.$$

A table of definite integrals shows

$$\int_0^\infty xe^{-ax^2}dx = \frac{1}{2a}$$

so

$$\langle v_x \rangle = 2N\left(\frac{1}{2\alpha}\right) = \frac{N}{\alpha}$$

Substituting our definitions for N and α produces

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_BT}\right)^{1/2}\left(\frac{2k_BT}{m}\right) = \left(\frac{2k_BT}{\pi m}\right)^{1/2}$$

This expression indicates the average speed for motion in one direction.

It is important to note that equation 1.2.1 describes the distribution function for one component of the molecular ***velocity***. Because a molecule is able to move in a positive or a negative direction, the range of one component of the molecular velocity (v_x in this case) is $-\infty$ to ∞. This distribution of velocities is a Gaussian distribution of velocities, as shown in Figure 27.2.1 .

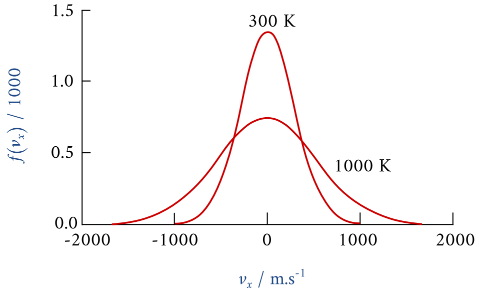

Figure 27.2.1 : Distribution of the x component of the velocity of a nitrogen molecule at 300 K and 1000 K. (CC BY-NC; Ümit Kaya via LibreTexts)

We will find in section 27.3 that the distribution of molecular ***speeds*** is not a Gaussian distribution.

Contributors and Attributions

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)
- Tom Neils (Grand Rapids Community College, editing)

1.3: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution

1.3.1: The Boltzmann Distribution

If we were to plot the number of molecules whose velocities fall within a series of narrow ranges, we would obtain a slightly asymmetric curve known as a *velocity distribution*. The peak of this curve would correspond to the *most probable* velocity. This velocity distribution curve is known as the *Maxwell-Boltzmann distribution*, but is frequently referred to only by Boltzmann's name. The **Maxwell-Boltzmann distribution law** was first worked out around 1860 by the great Scottish physicist, **James Clerk Maxwell** (1831-1879), who is better known for discovering the laws of electromagnetic radiation. Later, the Austrian physicist **Ludwig Boltzmann** (1844-1906) put the relation on a sounder theoretical basis and simplified the mathematics somewhat. Boltzmann pioneered the application of statistics to the physics and thermodynamics of matter and was an ardent supporter of the atomic theory of matter at a time when it was still not accepted by many of his contemporaries.

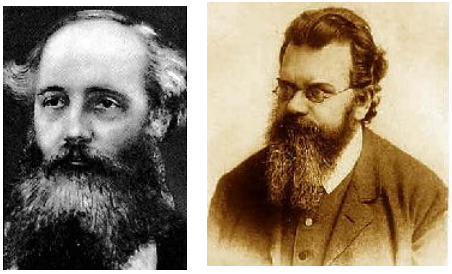

Figure 27.3.1 : Maxwell (left) and Boltzmann (right) are responsible for describing the velocity distribution of gas molecules

In section 27.2 we saw that the distribution function for molecular speeds in the x direction is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}}$$

However, real gas samples have molecules not only with a distribution of molecular speeds and but also a random distribution of directions. Using normal vector magnitude properties (or simply using the Pythagorean Theorem), it can be seen that

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

Since the direction of travel is random, the velocity can have any component in x, y, or z directions with equal probability. As such, the average value of the x, y, or z components of velocity should be the same. And so

$$\langle v \rangle^2 = 3\langle v_x \rangle^2$$

Substituting this into the expression for pressure yields

$$p = \frac{N_{tot} m}{3V} \langle v \rangle^2$$

All that remains is to determine the form of the distribution of velocity magnitudes the gas molecules can take. In his 1860 paper (Illustrations of the dynamical theory of gases. Part 1. On the motions and collisions of perfectly elastic spheres, 1860), Maxwell proposed a form for this distribution of speeds which proved to be consistent with observed properties of gases (such as their viscosities). He derived this expression based on a transformation of coordinate system from Cartesian coordinates (x, y, z) to spherical polar coordinates (v, θ, ϕ). In this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\, dy\, dz = v^2 \sin(\theta)\, dv\, d\theta\, d\phi$$

Applying this transformation of coordinates **Maxwell's distribution** took the following form

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \tag{1.3.1}$$

The Distribution of Speed over all Directions

The Distribution of Kinetic Energy in Three Dimensions

As noted above, the distribution function of molecular energies for one dimension is

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

To obtain a three-dimensional probability distribution, you multiply the distribution function for each of the three dimensions so that

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

given

$$\langle v\rangle^2 = \langle v_x\rangle^2 + \langle v_y\rangle^2 + \langle v_z\rangle^2$$

The Conversion of Energy Distribution to Speed Distribution

To convert the three-dimensional energy distribution to a speed distribution over all space, the energy distribution must be summed over all directions. This sum is usually described by imagining a "velocity space" in spherical polar coordinates. As noted above, in this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\, dy\, dz = v^2 \sin(\theta)\, dv\, d\theta\, d\phi$$

You integrate over θ and ϕ to sum over all space, thus

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \underbrace{\int_0^{\pi} \int_0^{2\pi} v^2 \sin\theta d\phi d\theta}_{=4\pi v^2}$$

This equation is rearranged to give

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

This function can be thought of as having three basic parts to it: **a normalization constant** (N), a velocity dependence (v^2), and an exponential term that contains the kinetic energy (½mv^2).

Because the function represents the fraction of molecules with the speed v, the sum of the fractions for all possible velocities must be unity. This sum can be calculated as an integral. The normalization constant ensures that

$$\int_0^{\infty} f(v) dv = 1$$

Thus the normalization constant is

$$N = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}$$

1.3.2: Velocity distributions depend on temperature and mass

Higher temperatures allow a larger fraction of molecules to acquire greater amounts of kinetic energy, causing the Boltzmann plots to spread out. Figure 27.3.2 shows how the Maxwell-Boltzmann distribution is affected by temperature. At lower temperatures, the molecules have less energy. Therefore, the speeds of the molecules are lower and the distribution has a smaller range. As the temperature of the molecules increases, the distribution flattens out. Because the molecules have greater energy at higher temperature, the molecules are moving faster.

Notice how the left ends of the plots are anchored at zero velocity (there will always be a few molecules that happen to be at rest.) As a consequence, the curves flatten out as the higher temperatures make additional higher-velocity states of motion more accessible. The area under each plot is the same for a constant number of molecules.

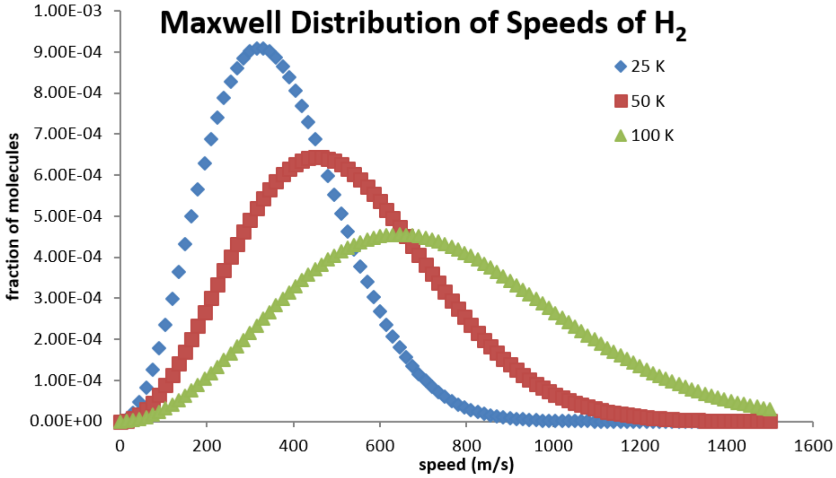

Figure 27.3.2: Maxwell Distribution of speeds for hydrogen molecules at differing temperatures.

Calculating the Average Speed

Using the Maxwell distribution as a distribution of probabilities, the average molecular speed in a sample of gas molecules can be determined.

$$\begin{aligned}\langle v\rangle &= \int_{-\infty}^{\infty} v\, f(v) dv \\ &= \int_{-\infty}^{\infty} v\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{-mv^2}{2k_BT}\right) dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^3 \exp\left(\frac{-mv^2}{2k_BT}\right) dv\end{aligned}$$

The following can be found in a table of integrals:

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

So

$$\langle v\rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1}{2\left(\frac{m}{2k_BT}\right)^2}\right]$$

Which simplifies to

$$\langle v\rangle = \left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

Note: the value of $\langle v\rangle$ is twice that of $\langle v_x\rangle$ which was derived in an earlier example!

$$\langle v\rangle = 2\langle v_x\rangle$$

✓ Example 27.3.1 :

What is the average value of the squared speed according to the Maxwell distribution law?

Solution:

$$\begin{aligned}\langle v^2\rangle &= \int_{-\infty}^{\infty} v^2\, f(v)dv \\ &= \int_{-\infty}^{\infty} v^2\, 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3}\, v^2 \exp\left(\frac{-mv^2}{2k_BT}\right)\, dv \\ &= 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3} \int_{-\infty}^{\infty} v^4 \exp\left(\frac{-mv^2}{2k_BT}\right)\, dv\end{aligned}$$

A table of integrals indicates that

$$\int_0^{\infty} x^{2n}e^{-ax^2}dx = \frac{1\cdot 3\cdot 5\ldots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$$

Substitution (noting that $n = 2$) yields

$$\langle v^2\rangle = 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3}\left[\frac{1\cdot 3}{2^3\left(\frac{m}{2k_BT}\right)^2}\sqrt{\frac{\pi}{\left(\frac{m}{2k_BT}\right)}}\right]$$

which simplifies to

$$\langle v^2\rangle = \frac{3k_BT}{m}$$

Note: The square root of this average squared speed is called the **root mean square** (RMS) speed, and has the value

$$v_{rms} = \sqrt{\langle v^2\rangle} = \left(\frac{3k_BT}{m}\right)^{1/2}$$

All molecules have the same kinetic energy (½mv^2) at the same temperature, so the fraction of molecules with higher velocities will increase as m, and thus the molecular weight, decreases. Figure 27.3.3 shows the dependence of the Maxwell-Boltzmann distribution on molecule mass. On average, heavier molecules move more slowly than lighter molecules. Therefore, heavier molecules will have a smaller speed distribution, while lighter molecules will have a speed distribution that is more spread out.

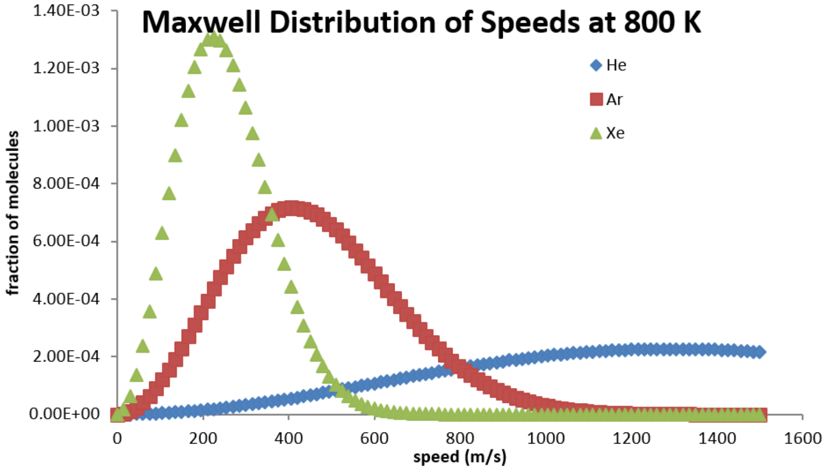

Figure 27.3.3: Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses.

1.3.3: Related Speed Expressions

Usually, we are more interested in the speeds of molecules rather than their component velocities. The Maxwell–Boltzmann distribution for the speed follows immediately from the distribution of the velocity vector, above. Note that the speed of an individual gas particle is:

$$v = \sqrt{v_x^2 + v_y^2 = v_z^2}$$

Three speed expressions can be derived from the Maxwell-Boltzmann distribution:

- the most probable speed,
- the average speed, and
- the root-mean-square speed.

The **most probable speed** is the maximum value on the distribution plot (Figure 27.3.4). This is established by finding the velocity when the derivative of Equation 1.3.1 is zero

$$\frac{df(v)}{dv} = 0$$

which is

$$v_{mp} = \sqrt{\frac{2RT}{M}} \tag{1.3.2}$$

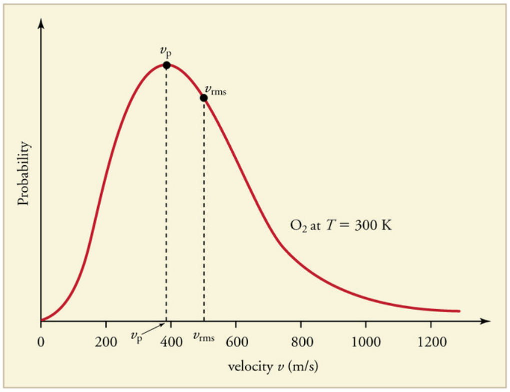

Figure 27.3.4 : The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures. from OpenStax. The speed at the top of the curve is called the most probable speed because the largest number of molecules have that speed.

The **average speed** is the sum of the speeds of all the molecules divided by the number of molecules.

$$v_{avg} = \bar{v} = \int_0^\infty v f(v) dv = \sqrt{\frac{8RT}{\pi M}}$$

The **root-mean-square speed** is square root of the average speed-squared.

$$v_{rms} = \bar{v^2} = \sqrt{\frac{3RT}{M}}$$

where

- R is the gas constant,
- T is the absolute temperature and
- M is the molar mass of the gas.

It *always* follows that for gases that follow the Maxwell-Boltzmann distribution:

$$v_{mp} < v_{avg} < v_{rms}$$

1.3.4: Problems

1. Using the Maxwell-Boltzman function, calculate the fraction of argon gas molecules with a speed of 305 m/s at 500 K.
2. If the system in problem 1 has 0.46 moles of argon gas, how many molecules have the speed of 305 m/s?

3. Calculate the values of C_{mp}, C_{avg}, and C_{rms} for xenon gas at 298 K.
4. From the values calculated above, label the Boltzmann distribution plot with the approximate locations of (C_{mp}\), C_{avg}, and C_{rms}.
5. What will have a larger speed distribution, helium at 500 K or argon at 300 K? Helium at 300 K or argon at 500 K? Argon at 400 K or argon at 1000 K?

1.3.4.1: Answers

1. 0.00141
2. 3.92×10^{20} argon molecules
3. c_{mp} = 194.27 m/s, c_{avg} = 219.21 m/s, c_{rms} = 237.93 m/s
4. As stated above, C_{mp} is the most probable speed, thus it will be at the top of the distribution curve. To the right of the most probable speed will be the average speed, followed by the root-mean-square speed.
5. Hint: Use the related speed expressions to determine the distribution of the gas molecules: helium at 500 K. helium at at 300 K. argon at 1000 K.

1.3.5: Sources

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Contributors and Attributions

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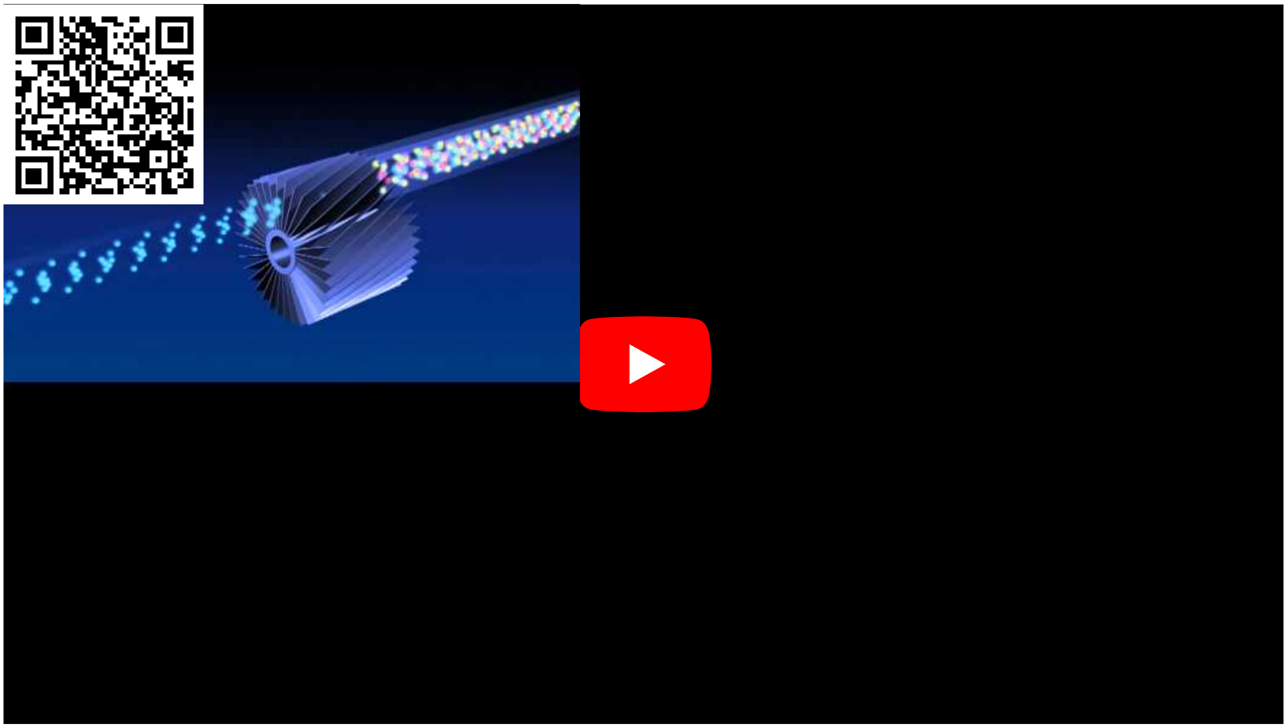
1.4: The Maxwell-Boltzmann Distribution Has Been Verified Experimentally

The Maxwell-Boltzman distruction distribution has been verified experimentally by a device called a velocity selector, which is essentially a series of spinning wheels with a hole through which the gas is effused. This ensures that only gas particles with a certain velocity will pass through all the holes as the wheels are spun at various rates. Thus it is possible to count the number of particles with various velocities and show that, indeed they do satisfy the Maxwell-Boltzmann distribution.



1.5: The Frequency of Collisions with a Wall

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the "collision volume".

$$V_{col} = v_x \Delta t \cdot A$$

in which the product of the velocity v_x and a time interval Δt is multiplied by A, the area of the wall with which the molecules collide.

All of the molecules within this volume, and with a velocity such that the x-component exceeds v_x (and is positive) will collide with the wall. That fraction of molecules is given by

$$N_{col} = \frac{N}{V} \frac{\langle v_x \rangle \Delta t \cdot A}{2}$$

and the frequency of collisions with the wall per unit area per unit time is given by

$$z_w = \frac{N}{V} \frac{\langle v_x \rangle}{2}$$

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

$$\langle v \rangle = \sqrt{\langle v_x \rangle + \langle v_y \rangle + \langle v_z \rangle}$$

and that

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle$$

it can be shown that

$$\langle v \rangle = 2 \langle v_x \rangle$$

or

$$\langle v_x \rangle = \frac{1}{2} \langle v \rangle$$

and so

$$z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

A different approach to determining z_w is to consider a collision cylinder that will enclose all of the molecules that will strike an area of the wall at an angle θ and with a speed v in the time interval dt. The volume of this collision cylinder is the product of its base area (A) times its vertical height ($v\cos\theta dt$), as shown in figure $1.5.1$.

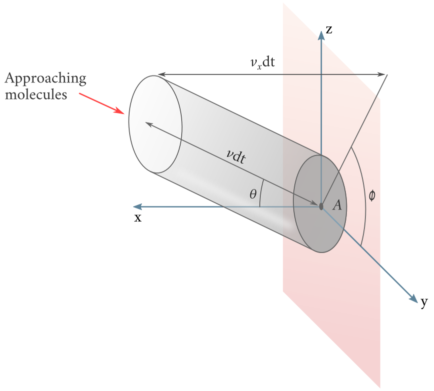


Figure $1.5.1$: The collision cylinder for determining the number of collisions of gas molecules with a wall. (CC BY-NC; Ümit Kaya)

The number of molecules in this cylinder is $\rho \cdot A \cdot v \cdot \cos\theta dt$, where ρ is the number density $\frac{N}{V}$. The fraction of molecules that are traveling at a speed between v and $v + dv$ is $F(v)dv$. The fraction of molecules traveling within the solid angle bounded by θ and $\theta + d\theta$ and between ϕ and $\phi + d\phi$ is $\frac{\sin\theta d\theta d\phi}{4\pi}$. Multiplying these three terms together results in the number of molecules colliding with the area A from the specified direction during the time interval dt

$$dN_w = \rho \cdot A \cdot v \cdot \cos\theta \, dt \, \cdot \, F(v)dv \cdot \frac{\sin\theta d\theta d\phi}{4\pi}$$

This equation can be rearranged to obtain

$$\frac{1}{A}\frac{dN_w}{dt} = \frac{\rho}{4\pi} vF(v)dv \cdot \cos\theta \sin\theta \, d\theta d\phi = dz_w$$

Integrating this equation over all possible speeds and directions (on the front side of the wall only), we get

$$z_w = \frac{\rho}{4\pi} \int_0^\infty vF(v)dv \cdot \int_0^{\pi/2} \cos\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

The result is that

$$z_w = \frac{1}{A}\frac{dN_w}{dt} = \frac{1}{4}\frac{N}{V}\langle v\rangle = \rho\frac{\langle v\rangle}{4} \tag{1.5.1}$$

Example 27.4.1

Calculate the collision frequency per unit area (Z_w) for oxygen at 25.0°C and 1.00 bar using equation 1.5.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Solution

N molecules = N_A x n, so that

$$\frac{N}{V} = \frac{(N_A) \cdot n}{V} = \frac{(N_A) \cdot P}{R \cdot T}$$

$$\frac{(6.022x10^{23}\,mole^{-1})(1.00\,bar)}{(0.08319\,L \cdot bar \cdot mole^{-1} \cdot K^{-1})(298\,K)} = 2.43 \times 10^{22}\,L^{-1} = 2.43 \times 10^{25}\,m^{-3}$$

and

$$\langle v\rangle = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8(8.314J \cdot K^{-1} \cdot mol^{-1})(298K)}{\pi \cdot (0.031999\,kg)}\right)^{\frac{1}{2}} = 444\,m \cdot s^{-1}$$

Thus

$$z_w = \frac{1}{4}(2.43 \times 10^{25} m^{-3})(444\,m \cdot s^{-1})\left(\frac{1\,m}{100\,cm}\right)^2 = 2.70 \times 10^{23} s^{-1} \cdot cm^{-2}$$

The factor of N/V is often referred to as the “number density” as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately 2.43 x 10^{19} molecule/cm^3. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm^3.

Exercise 27.4.1

Calculate the collision frequency per unit area (Z_w) for hydrogen at 25.0°C and 1.00 bar using equation 1.5.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Answer

$$\langle v \rangle = 1770\, m \cdot s^{-1}$$

and

$$Z_w = 1.08 \times 10^{24} s^{-1} \cdot cm^{-2}$$

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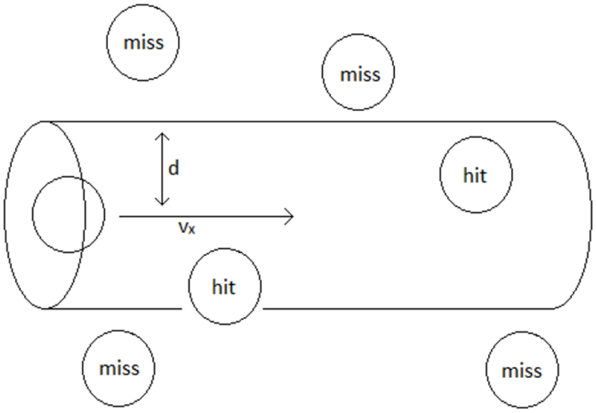
9.14: Collisions with Other Molecules

A major concern in the design of many experiments is collisions of gas molecules with other molecules in the gas phase. For example, molecular beam experiments are often dependent on a lack of molecular collisions in the beam that could degrade the nature of the molecules in the beam through chemical reactions or simply being knocked out of the beam.

In order to predict the frequency of molecular collisions, it is useful to first define the conditions under which collisions will occur. For convenience, consider all of the molecules to be spherical and in fixed in position except for one which is allowed to move through a "sea" of other molecules. A molecular collision will occur every time the center of the moving molecule comes within one molecular diameter of the center of another molecule.



One can easily determine the number of molecules the moving molecule will "hit" by determining the number of molecules that lie within the "collision cylinder". Because we fixed the positions of all but one of the molecules, we must use the relative speed of the moving molecule, which will be given by

$$v_{rel} = \sqrt{2} \times v$$

The volume of the collision cylinder is given by

$$V_{col} = \sqrt{2}\, v \,\Delta t\, A$$

The **collisional cross section**, which determined by the size of the molecule is given by

$$\sigma = \pi d^2$$

Some values of σ are given in the table below:

Table 2.6.1: Collisional cross-section of Select Species

Molecule	**σ (nm^2)**
He	0.21
Ne	0.24
N_2	0.43
CO_2	0.52
C_2H_4	0.64

Since the number of molecules within the collision cylinder is given by

$$N_{col} = \frac{N}{V} V_{col}$$

and since the number density (N/V) is given by

$$\frac{N}{V}=\frac{p}{k_BT}$$

the number of collisions is given by

$$N_{col}=\frac{p}{k_BT}(\sqrt{2}\,v\Delta t\sigma)$$

The frequency of collisions (number of collisions per unit time) is then given by

$$Z=\frac{\sqrt{2}p\sigma}{k_BT}\langle v\rangle$$

Perhaps a more useful value is the **mean free path** (λ), which is the distance a molecule can travel on average before it collides with another molecule. This is easily derived from the collision frequency. How far something can travel between collisions is given by the ratio of how fast it is traveling and how often it hits other molecules:

$$\lambda=\frac{\langle v\rangle}{Z}$$

Thus, the mean free path is given by

$$\lambda=\frac{k_BT}{\sqrt{2}p\sigma}$$

The mere fact that molecules undergo collisions represents a deviation from the kinetic molecular theory. For example, if molecules were infinitesimally small ($\sigma\approx 0$) then the mean free path would be infinitely long! The finite size of molecules represents one significant deviation from ideality. Another important deviation stems from the fact that molecules do exhibit attractive and repulsive forces between one another. These forces depend on a number of parameters, such as the distance between molecules and the temperature (or average kinetic energy of the molecules.)

9.15: Mean Free Path

9.15.1: Collision energy

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

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} \tag{9.15.1}$$

We can describe kinetic energy in terms of center-of-mass $(\mathbf{P})$ and relative momentum $(\mathbf{p})$, which are given by

$$\mathbf{P} = \mathbf{p}_A + \mathbf{p}_B$$

and

$$\begin{aligned} \mathbf{p} &= \text{relative velocity} \times \mu \\ &= (\mathbf{v}_A - \mathbf{v}_B) \times \left(\frac{m_A m_B}{m_A + m_B}\right) \\ &= \frac{m_B \mathbf{p}_A - m_A \mathbf{p}_B}{M} \end{aligned}$$

where

$$M = m_A + m_B$$

is the total mass of the two particles, and

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

is the **reduced mass** of the two particles.

Substituting these terms into equation 9.15.1, we find

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

Note that the kinetic energy separates into a sum of a center-of-mass term and a relative momentum term.

Now the relative position of the two particles 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, which is mass independent, we get

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

which is called the *collision energy*

9.15.2: 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. 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

$$\sigma_A = \pi d_A^2, \quad \sigma_B = \pi d_B^2$$

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

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

and the resulting collision cross section becomes

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

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

9.15.3: 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 27.6.1). If the system has a number density ρ, then the number of collisions that will occur is

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

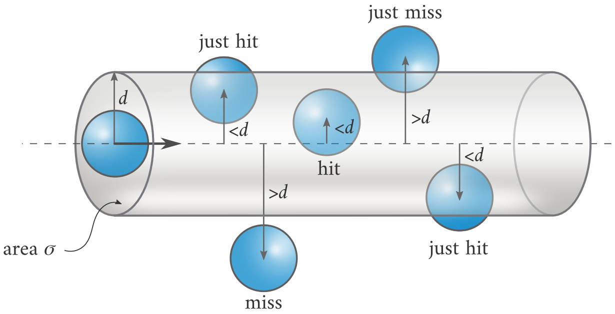


Figure 27.6.1 : Collision cylinder. Any particle that partially overlaps with this volume will experience a collision with a test particle tracing out this volume. (CC BY-NC; Ümit Kaya)

We define the collision frequency for a single molecule, z_A, also known as the average collision rate as $N_{\text{coll}}/\Delta t$, i.e.,

$$z_A=\frac{N_{\text{coll}}}{\Delta t}=\frac{\rho\sigma l}{\Delta t}=\rho\sigma\langle v\rangle \tag{9.15.2}$$

where $\langle v\rangle$ is the average speed of a particle

$$\langle v\rangle=\sqrt{\frac{8k_BT}{\pi m_A}}$$

Equation 9.15.2 is not quite correct because it is based on the assumption that only the molecule of interest is moving. If we take into account the fact that all of the particles are moving relative to one another, and assume that all of the particles are of the same type (say, type A), then performing the average over a Maxwell-Boltzmann speed distribution gives

$$\langle v_r\rangle=\sqrt{\frac{8k_BT}{\pi\mu}}$$

where $\mu = m_A/2$ is the reduced mass.

Thus,

$$\langle v_r \rangle = \sqrt{2} \langle v \rangle$$

and

$$z_A = \sqrt{2}\rho\sigma\langle v \rangle \;= \rho\sigma\langle v_r \rangle$$

The reciprocal of z_A is a measure of the average time between collisions for a single molecule.

9.15.4: Mean Free Path

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

$$\lambda = \frac{\langle v \rangle}{\sqrt{2}\rho\sigma\langle v \rangle} = \frac{1}{\sqrt{2}\rho\sigma}$$

The mean free path can also be described using terms from the ideal gas law, because $\rho = \dfrac{P \cdot N_A}{R \cdot T}$:

$$\lambda = \frac{R \cdot T}{\sqrt{2} \cdot N_A \cdot \sigma \cdot P}$$

9.15.5: 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 $9.15.2$ Such a path is often referred to as a *random walk path*.

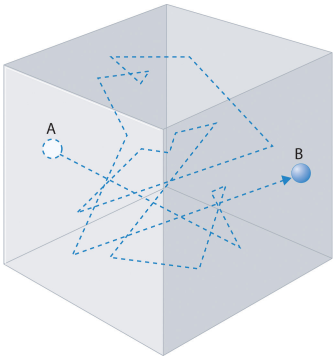


Figure $9.15.2$: Random walk path. The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

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

$$j = N - i = N - (j + k) = N - j - k$$

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

$$i = N - j = N - (i - k) = N - i + k$$

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

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

We now take the logarithm of both sides:

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

and use Stirling's approximation:

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

and write $\ln P(k)$ as

$$\begin{aligned} \ln P(k) & \approx N \ln N - N - N \ln 2 - \frac{1}{2}(N+k) \ln \frac{1}{2}(N+k) + \frac{1}{2}(N+k) - \frac{1}{2}(N-k) \ln \frac{1}{2}(N-k) + \frac{1}{2}(N-k) \\ & = N \ln N - N \ln 2 + \frac{1}{2}(N+k) \ln \frac{1}{2} - \frac{1}{2}(N+k) \ln (N+k) - \frac{1}{2}(N-k) \ln \frac{1}{2} - \frac{1}{2}(N-k) \ln (N-k) \\ & = N \ln N - N \ln 2 + \frac{1}{2}(N+k) \ln 2 - \frac{1}{2}(N+k) \ln (N+k) + \frac{1}{2}(N-k) \ln 2 - \frac{1}{2}(N-k) \ln (N-k) \\ & = N \ln N - \frac{1}{2}[(N+k) \ln (N+k) + (N-k) \ln (N-k)] \end{aligned}$$

Now, write

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

and

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

We now use the expansions

$$\begin{aligned} \ln \left(1 + \frac{k}{N}\right) & = \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots \\ \ln \left(1 - \frac{k}{N}\right) & = -\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots \end{aligned}$$

If we stop at the second-order term, then

$$\begin{aligned} \ln P(k) & = N \ln N - \frac{1}{2}(N+k)\left[\ln N + \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] - \frac{1}{2}(N-k)\left[\ln N - \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\ & = -\frac{1}{2}(N+k)\left[\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] + \frac{1}{2}(N-k)\left[\left(\frac{k}{N}\right) + \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\ & = \frac{1}{2} N \left(\frac{k}{N}\right)^2 - k\left(\frac{k}{N}\right) \\ & = \frac{k^2}{2N} - \frac{k^2}{N} = -\frac{k^2}{2N} \end{aligned}$$

so that

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

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

$$P(x) = \frac{1}{L\sqrt{2\pi}}\, e^{-x^2/2L^2} = \frac{1}{\sqrt{2\pi N\lambda^2}}\, e^{-x^2/2N\lambda^2} \tag{9.15.3}$$

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

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

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

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

Note that this distribution satisfies the following equation:

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

which is called the diffusion equation. The diffusion equation is, in fact, more general than the Gaussian distribution in Equation 9.15.3. 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:

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

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

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

9.15.6: Total collision frequency per unit volume

In equation 27.6.18, z_A represents the collision frequency for one specific molecule in a gas sample. If we wish to calculate the total collision frequency per unit volume, the number density of the molecules, ρ, must be taken into account. The total collision frequency in a sample that contains only A molecules, Z_{AA}, is

$$Z_{AA} = \frac{1}{2}\rho z_A = \frac{1}{2}\sigma\langle v_r\rangle\rho^2 = \frac{\sigma\langle v\rangle\rho^2}{\sqrt{2}}$$

The factor of $\frac{1}{2}$ must be included to avoid double counting collisions between similar molecules. (This is identical reasoning to the fact that there is only one way to roll double 3 with two dice.)

If you have a gas sample that contains A molecules and B molecules, then

$$Z_{AB} = \sigma_{AB}\langle v_r\rangle\rho_A\rho_B \tag{9.15.4}$$

where

$$\sigma_{AB} = \pi\left(\frac{d_A+d_B}{2}\right)^2 \text{ and } \langle v_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

✓ Example 9.15.1

Calculate the frequency of hydrogen-hydrogen collisions in a 1.00 cubic centimeter container at 1.00 bar and 298 K.

Solution

The collisional frquency requires knowledge of (1) the number denisty, the average speed (Equation 9.15.4).

The value of σ_{H_2} is 2.30 x 10^{-19} m^2.

The number density:

$$\rho = \left(\frac{N_A P_{H_2}}{RT}\right) = \left(\frac{(6.022x10^{23} mole^{-1})(1.00 \text{ bar})}{(0.08314 L \cdot bar \cdot mol^{-1} \cdot K^{-1})(298 K)}\right) = 2.43 \times 10^{22} L^{-1} = 2.43 \times 10^{25} m^{-3} \tag{9.15.5}$$

The average speed:

$$\langle \text{v} \rangle = \sqrt{\frac{8\text{R T}}{\pi \text{M}}} = \sqrt{\left(\frac{8(8.314 J \cdot K^{-1})(298 K)}{\pi(0.002016 kg)}\right)} = 1770 \frac{m}{s} \tag{9.15.6}$$

These are substituted into Equation 9.15.4 to get the collisional frequency

$$\begin{aligned} Z_{H_2,H_2} &= \frac{(2.30x10^{-19} m^2)(1770 \frac{m}{s})(2.43x10^{25} m^{-3})^2}{\sqrt{2}} \\ &= 1.7x10^{35} s^{-1} m^{-3} \\ &= 1.7 \times 10^{29} s^{-1} cm^{-3} \end{aligned}$$

1.5: The meaning and measurement of temperature

One of the key ways that we will need to describe energy is in direct connection to the temperature of a system. One of the foundational ideas of *statistical mechanics* is a model for the behavior of gas molecules called the *kinetic theory of gases* - it's a model built on considering the particles in a gas to be very small, noninteracting, and colliding in perfectly elastic ways. ([The Wikipedia article on the kinetic theory](https://en.wikipedia.org/wiki/Kinetic_theory_of_gases) is a wonderful primer with a very understandable derivation.) The kinetic theory also provides our first definition of temperature, which is *a measure of the average kinetic energy of the particles of a gas at a state of thermal equilibrium*. Mathematically, that measure is

$$T = \frac{2K_{tot}}{3Nk_B}\text{Units: K}$$

We can prove this result with the kinetic theory, but we will take it as a definition for now. The average kinetic energy is hidden in the expression of total kinetic energy divided by N, the count of molecules present.

This forces the units of the genuinely new quantity k_B to be Joules per Kelvin. This is a constant, our first of the course; it is known as the *Boltzmann constant*, after the German thermodynamics scholar Ludwig Boltzmann who first described it:

$$k_B = 1.38065 \times 10^{-23}\ \text{J K}^{-1}$$

We will explore the meaning of this constant and its connection to other ideas in thermodynamics as we move forward in the course. Multiplying k_B by temperature gives units of energy, and it is not uncommon when talking about the energy of individual molecules to describe their energy in units of k_BT.

The direct proportionality between average kinetic energy of molecules and temperature also enforces a system of measuring temperature where the temperature is zero when the average kinetic energy of all molecules is zero - a circumstance whose existence is only theoretical, never actually observed. It also enforces the impossibility of negative temperature. We call the Kelvin scale an *absolute* scale for that reason - every temperature is positive and has a neat proportional connection to properties of that gas. No other temperature scale has such a neat proportional connection, which is why - even though the Celsius scale and the Fahrenheit scale are convenient to use for other reasons, we will overwhelmingly prefer the Kelvin scale when doing thermodynamic calculations.

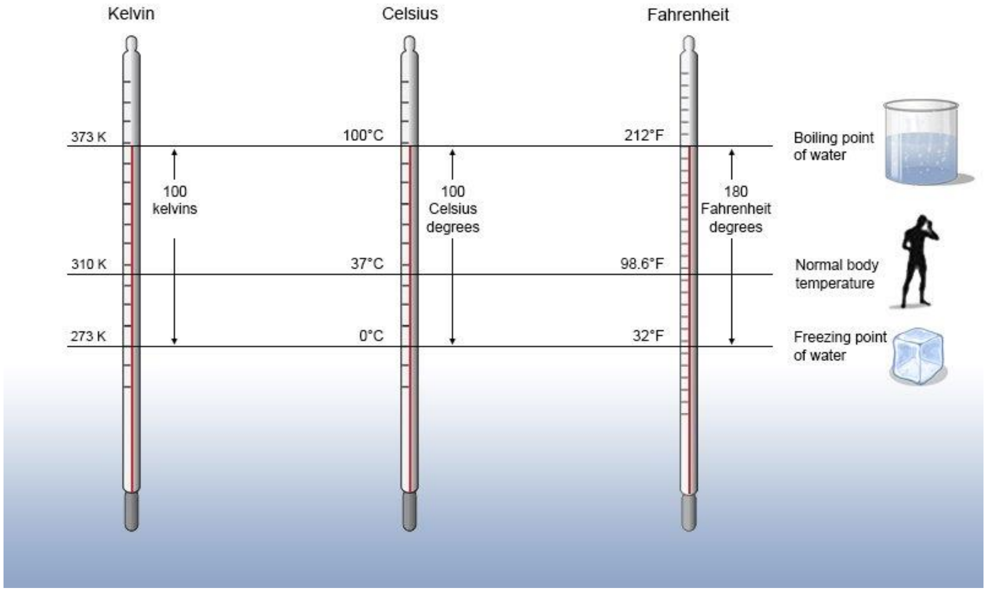


Image from [Community College Consortium for Bioscience Credentials](https://www.ccbcmd.edu); [CC BY 3.0](https://creativecommons.org/licenses/by/3.0/).

It's worth a reminder of how the Celsius and Fahrenheit scales are structured compared to the Kelvin scale. Celsius was deliberately scaled to have 100 degrees between the freezing and boiling points of water; the Celsius scale was set prior to the Kelvin scale, and the value of the Boltzmann constant turns out to be dependent upon an absolute temperature scale where there are 100 units of temperature between the freezing and boiling point of water. The development of the Fahrenheit scale is more obscure, but the original intent was to set temperatures so that the normal body temperature is 100 degrees. It also turns out to be more convenient to define Fahrenheit based on freezing and boiling points of water, however.

1.6: The variables of state, pressure units, and the ideal gas law

Temperature is only one of the key ways that we can describe the properties of a gas. Counting up the number of molecules - or, more reasonably, the number of *moles* - is another.

These are two of the four conventional *variables of state* (or *state variable*) for a gas. The variables of state are considered the ways of describing the *entire* condition of an ideal gas.

State variable	**Symbol**	**SI Unit (mks)**	**Abbreviation**	**Base SI units**
Temperature	T	Kelvin	K	K
Count of substance	n	moles	mol	mol
Volume	V	cubic meters	m^3	m^3
Pressure	P	Pascals	Pa	$kg\ m^{-1}\ s^{-2}$ (or $N\ m^{-2}$)

Volume units are very straightforward; they're length units in three dimensions, in keeping with a volume being proportional to any length dimension of an object cubed. Of course, the base SI units for volume, cubic *meters*, are *very* large indeed; nobody would actually want to lift a cube of anything that was a meter of length on each side. This is why most small-scale exercises will set units of volume to cubic *centi*meters, or the size of a cube 1 centimeter on each side; this is much more manageable.

Many modern physical chemistry textbooks will make mention of a cubic *deci*meter, the size of a cube 1 decimeter (or 10 centimeters) on each side. 1 dm^3 is just another way to describe one *liter*, which is the common metric unit of volume. Because of the cubing of 10, there are 1000 liters in a cubic meter; there are 1000 cubic centimeters in a liter, which is why the cubic centimeter and the milliliter are frequently equated with one another.

$$1\ \mathrm{L} = 1\ \mathrm{dm}^3 = 1000\ \mathrm{cm}^3 = 1000\ \mathrm{mL} 1\ \mathrm{m}^3 = 1000\ \mathrm{dm}^3 = 1000\ \mathrm{L}$$

Pressure units are much more plentiful, and much more convoluted. *Pressure* is defined simply as a force per unit area. The base SI unit of pressure is the *Pascal*, which is equivalent to SI measure of force (the Newton) divided by the SI measure of surface area (the square meter). This is a *very* small unit of pressure, approximately one-one hundred thousandth normal atmospheric pressure.

Historically standard atmospheric pressure has been defined by the height of a column of mercury that is supported by that pressure, in the nature of an experiment designed by one of Galileo Galiei's apprentices, Evangelista Torricelli. In his honor, a height of 1 millimeter of mercury in a barometric column is called a *torr*; standard atmospheric pressure, also known as *one atmosphere*, is equivalent to a height of 760 mm of mercury in this kind of column; this turns out to be about 101,300 Pascals (or 101.3 kiloPascals).

Most chemists use the atmosphere as their reference atmospheric pressure, but some prefer a truly metric unit, the *bar*, which is set to exactly 100,000 Pascals (exactly 100 kPa). Meterological pressure is frequently communicated in *millibars*.

$$1\ \mathrm{atm} = 760\ \mathrm{torr} = 1.013\ \mathrm{bar} = 101\ 300\ \mathrm{Pa} 1\ \mathrm{bar} = 750.2\ \mathrm{torr} = 0.9872\ \mathrm{atm} = 100\ 000\ \mathrm{Pa}$$

For reasons that are purely historic, we will prefer the atmosphere as our units of pressure - but there will be times when any of the four will be preferable. Vapor pressures are far more frequently communicated in torr (which, again, is the same thing as mm Hg). When we do computations in base-SI units, we will need Pascals; and again, bars are metric derivations from the Pascal. Atmospheres are simply most frequently used and most easily explained - a multiple of normal atmospheric pressure.

If we take the kinetic theory's two conditions of *ideality* of gases - the essentially zero volume of the gas molecules, and the lack of attraction or repulsion between gas molecules - as valid, we find that the ratio of pressure times volume of an ideal gas to number of moles times temperature is a *constant*:

$$R = \frac{PV}{nT} R = 0.082058 \mathrm{L\ atm\ mol}^{-1} \mathrm{K}^{-1} = 8.31447 \mathrm{J\ mol}^{-1} \mathrm{K}^{-1}$$

This is the equation more commonly written as $PV = nRT$, the ideal gas law. R, like the value of k_B, is a constant that will turn up every now and again in our computations. Like the definition of temperature, we *can* derive this law from first physical principles; however, this is a familiar enough statement to us that we will simply take it as something we know, as a straightforward starting point.

There's one additional thing to note about these two constants we've worked with, the value of k_B and the value of R. You see a hint of that thing in the exponent on the value of k_B, the exponent of 10^{-23}. Divide the value of R by the value of k_B and make a note of what comes out:

$$\frac{R}{k_B}=\frac{8.31447\text{J mol}^{-1}\text{K}^{-1}}{1.38065\times 10^{-23}\text{J K}^{-1}}=6.0221\times 10^{23}\text{mol}^{-1}\rightarrow\frac{R}{k_B}=N_A$$

R and k_B are, in many ways, the exact same constant. R, on the one hand, deals with an energy per *mole* per Kelvin; k_B deals with an energy *per molecule* per Kelvin. The ratio of R to k_B is the familiar value of Avogadro's number; this connection can prove useful for us as we move forward.

1.7: Ideal vs. real gases and the van der Waals equation

Consider a simple application of the ideal gas law. Let's take an oxygen tank of rigid walls, with a fixed volume of 40.0 L. Let's maintain this tank at room temperature of 298 K. Let's fill this gas container with 1.000 kg of oxygen gas. We can show that this mass of oxygen corresponds to 31.25 moles of gas (prove this to yourself!). We can then use that number of moles, the volume of the tank, and the temperature to find the pressure the gas is under:

$$PV = nRT \rightarrow P = \frac{nRT}{V} = \frac{(31.25\text{mol})(0.082058\text{L atm mol}^{-1}\text{K}^{-1})(298\text{K})}{40.0\text{L}} = \mathbf{19.1\ atm}$$

Now think about the ideal gas law computation we've just completed. There's nothing in that computation that's dependent on the gas being oxygen at all; the only thing in the setup of that equation that did depend on the identity of the gas was determining that there was 31.25 mol of gas in 1.000 kg of oxygen. 31.25 moles of *any* gas, according to the ideal gas law, would apply a pressure of 19.1 atm on the walls of its container.

The ideal gas law, of course, is one of the great general chemistry fibs. It doesn't work in real life.

Now, it comes *close* to working in real life under the conditions we care about the most; relatively warm temperatures and relatively low pressures, conditions where the space between molecules is great and the molecules can zip past one another without substantial attraction or repulsion. We teach the ideal gas law not because it's a perfect description of how gases behave at all conditions, but because it comes acceptably close to describing how gases behave at the conditions we're most likely to experience, and it gives a passable first estimate even outside of those conditions. The ideal gas law clearly communicates that putting 1.000 kg of an elemental gas into a 40.0 L container is going to result in a *very* high pressure. Even if it's not a perfect computation, it's useful.

One of our first big theoretical hurdles is this: when we have conditions where the ideality of the gases isn't something we can assume, when the molecules are big and when the molecules attract one another substantially, how do we handle the correction?

There are two approaches we can take. We'll take the more rational approach first.

Think about the quantities of state. The number of molecules present - the count of moles - doesn't change when the attraction or the size of molecules changes. Neither does the kinetic energy - the assumptions of ideality of a gas have to do with the *size* of molecules, not the *mass*. So we can leave *n* and *T* alone when we correct for nonideality.

The size of the molecule obviously impacts *volume*. *V* in the ideal gas law works best, it turns out, when it represents the amount of space in the gas *not taken up by gas molecules*. When we go from molecules that are infinitely small to molecules that have real size, the volume of space available is going to be thrown off by that size, and thrown off more dramatically as the gas molecules get bigger. So we have to correct by subtracting out the amount of space taken up by the molecules, which we do this way:

$$V_{corr} = V - nb b\text{units: L mol}^{-1}$$

The correction we've introduced is a quantity called the *molar volume of gas molecules*, or simply the *van der Waals b constant*, after the Dutch thinker who developed this correction. The larger the size of the gas molecule, the larger *b* is. It's as straightforward as can be.

It also stands to reason that attraction or repulsion between molecules impacts pressure; the more gas molecules attract, the less the pressure is (because the attraction draws the molecules together and relieves the pressure), and the more gas molecules repel, the greater the pressure is (because the repulsion drives the molecules apart and pushes against the walls of the container). A corrected pressure that would fit the ideal gas law would add in a term that accounts for the magnitude of the attractive force between molecules. Unfortunately, developing a mathematical relationship for this term is not as straightforward as correcting the volume, because of the complex nature of that attraction even under conditions that remain close to ideality. The relationship that van der Waals developed to establish the value of his *van der Waals a constant* (which doesn't have a secondary name) is simply going to be described here without proof:

$$P_{corr} = P + \frac{n^2 a}{V^2} a\text{units: L}^2\text{atm mol}^{-2}$$

Therefore a full correction to the ideal gas law, which we call the *van der Waals equation*, keeps the *nRT* side intact but changes the left side substantially:

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT \text{van der Waals equation}$$

The values of *a* and *b* are unique based on the gas. Helium is the real gas closest to ideality, obviously because of its noble nature leading it to be not substantially attractive or repulsive, and because of its small single atom. Real gas attraction also has far more to do with size than molecular polarity, although obviously when gases are of comparable size more polar gases attract more than less.

Gas	**Chemical formula**	***a*** (L^2 atm mol^{-2})	***b*** (L mol^{-1})
Ammonia	NH_3	4.17	0.0371
Argon	Ar	1.34	0.0320
Carbon dioxide	CO_2	3.61	0.0429
Chlorine	Cl_2	6.25	0.0542
Fluorine	F_2	1.15	0.0290
Helium	He	0.0341	0.0238
Hydrogen	H_2	0.242	0.0265
Methane	CH_4	2.27	0.0430
Neon	Ne	0.205	0.0167
Nitrogen	N_2	1.39	0.0391
Oxygen	O_2	1.36	0.0319
Water	H_2O	5.46	0.0305

Table 3: van der Waals coefficients for selected gases. More complete data in the corresponding LibreTexts reference table.

Again, the corrections for a gas that has a low pressure and a high temperature are trivial. The major differences that you find between the ideal gas law and the van der Waals equation are computations that involve high pressure or those that involve low temperature.

Let's return to our example at the start. The ideal gas law gave us no way to distinguish 31.25 moles of oxygen from 31.25 moles of any other gas. The van der Waals equation, on the other hand, requires us to use values for *a* and *b* that are unique to oxygen, and allow us to correct for the size of the oxygen molecule and the interactions that happen between oxygen molecules. When we use the van der Waals equation to solve for the pressure inside this gas tank, we get an adjustment to the value we computed with the ideal gas law:

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT \rightarrow P=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}$$

$$\rightarrow P=\frac{(31.25\text{mol})(0.082058\text{L atm mol}^{-1}\text{K}^{-1})(298\text{K})}{40.0\text{L}-(31.25\text{mol})(0.0319\text{L mol}^{-1})}-\frac{(31.25\text{mol})^2(1.36\text{L}^2\text{atm mol}^{-2})}{(40.0\text{L})^2}$$

$$\rightarrow P=19.6\text{atm}-0.830\text{atm}=\mathbf{18.8atm}$$

This isn't a massive correction! The uncorrected ideal gas computation has less than a 2% error when compared to this "corrected" van der Waals calculation. But it does give a picture of how the attraction between oxygen molecules relieves the pressure that would be exerted on the container, because of the subtracting out of the *a*-term in the rearranged van der Waals equation.

As an exercise for yourself, repeat this both the ideal gas computation and the van der Waals compuation for 1.000 gram of oxygen gas in this container. This should give you a very low pressure in the container (0.0191 atm) that isn't corrected for by the van der Waals equation at any significance; this will further emphasize that there's need to correct for the ideal gas law when pressures are high, not when pressures are low.

1.8: Another way of dealing with real gases- the virial equation

The van der Waals equation is an improvement on the ideal gas law, but it still has weaknesses. More sophisticated equations (Redlich-Kwong and Peng-Robinson are the two most prominent) use the same basic underpinning of correcting the ideal gas law with terms that represent molecular volume and molecular attraction.

On the other hand, a rawer mathematical approach to describing deviations from ideality is to express those deviations as part of a polynomial series where the constants have less intentional physical meaning, but instead are simply fine-tuned corrections. These types of approaches are called *virial equations*, so named as they are expressions of the force between molecules.

The most fundamental of the virial equations multiplies the right side of the ideal gas law by a power series:

$$PV = nRT\left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \frac{n^3D}{V^3} + \cdots\right)$$

In this equation, *B*, *C*, and *D* (and all the values that would follow) are dubbed *virial coefficients*. In most practical applications, even a mere single correction using *B*, also known as the *second virial coefficient*, is sufficient:

$$PV = nRT\left(1 + \frac{nB}{V}\right)$$

Use of the third virial coefficient *C* and the fourth virial coefficient *D*, let alone further coefficients, are reserved only for specialized technical applications. (The first virial coefficient is in the first term of the parenthetical correction - simply 1 in all conditions.)

Gas	**If *T* = 100 K, B =**	**If *T* = 273 K, B =**	**If *T* = 373 K, B =**
Argon	-0.1870 L mol^{-1}	-0.0217 L mol^{-1}	-0.0042 L mol^{-1}
Helium	0.0114 L mol^{-1}	0.0120 L mol^{-1}	0.0113 L mol^{-1}
Hydrogen	-0.0020 L mol^{-1}	0.0137 L mol^{-1}	0.0156 L mol^{-1}
Neon	-0.0060 L mol^{-1}	0.0104 L mol^{-1}	0.0123 L mol^{-1}
Nitrogen	-0.1600 L mol^{-1}	-0.0105 L mol^{-1}	0.0062 L mol^{-1}
Oxygen	-0.1975 L mol^{-1}	-0.0220 L mol^{-1}	-0.0037 L mol^{-1}

Table 4: Second virial coefficients for selected gases as a function of temperature.
Data directly from the corresponding table in Monk's Physical Chemistry, with units converted.

Note that while *B* has units of L mol^{-1}, it is *not* the same as the van der Waals constant *b* and does *not* represent volume of molecules; this constant is an attempt to combine all the information included in the van der Waals *a* and *b* constants into a *single* value. For that reason, the meaning behind *B* is far more dependent on temperature than the van der Waals constants. The value of *B* for oxygen at 273 K is -0.0220 L mol^{-1}; however, that value approaches negligibility (at -0.0037 L mol^{-1}) at 373 K, and becomes far more significant (-0.198 L mol^{-1}) at 100 K.

It's not listed in the table above, but the value of *B* for oxygen at 298 K is -0.0158 L mol^{-1}. If we were to determine the volume correction for our kilogram (or 31.25 mol) of oxygen gas at standard ambient temperature, a solution of the simplified virial equation would give:

$$PV = nRT\left(1 + \frac{nB}{V}\right) \rightarrow P = \frac{nRT}{V}\left(1 + \frac{nB}{V}\right)$$

$$\rightarrow P = \frac{(31.25\text{mol})(0.082058\text{L atm mol}^{-1}\text{K}^{-1})(298\text{K})}{40.0\text{L}}\left(1 + \frac{(31.25\text{mol})(-0.0158\text{L mol}^{-1})}{40.0\text{L}}\right)$$

$$\rightarrow P = 19.1\text{atm}(1 - 0.0123) = \mathbf{18.9\ atm}$$

This is a correction very similar to that given by the van der Waals equation.

Because of the dependence on temperature that the virial coefficients show, virial coefficients are not traditionally tabulated simply. Papers and entire volumes are given over to the calculation of virial coefficients at a range of specific temperatures, and those coefficients are generally derived through gas behavior or empirically determined. Reliable approximations for many applications are genuinely valuable, and worth the price of a scientific text.

It's worth a mention, at the end of this particular discussion, that the quantity *n / V* turns up *repeatedly* in these equations, in the virial equation in particular. It's convenient to simplify this quantity, and we usually do so by creating a definition called the *molar volume* of a gas:

$$\overline{V} = \frac{V}{n} \text{units of} \overline{V} : \mathrm{L\ mol}^{-1}$$

This definition allows us to simplify the virial equation reasonably well:

$$PV = nRT\left(1 + \frac{nB}{V}\right) \rightarrow P\frac{V}{n} = RT\left(1 + \frac{n}{V}B\right) \rightarrow P\overline{V} = RT\left(1 + \frac{B}{\overline{V}}\right)$$

We can also apply this definition to the van der Waals equation, and achieve a similar simplification:

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

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

We will use this definition repeatedly to make our lives easier as we start to dig into the actual discipline of thermodynamics. Be aware that, for clarity's sake, I make a very deliberate nomenclature choice and write the molar quantity with a bar over the symbol. This choice will take other quantities that other textbooks are less clear about and help us understand more deeply.

1.9: Connecting the van der Waals and the viral equations- the Boyle temperature

Using the molar volume definition, we can rewrite the ideal gas law as a ratio that will always equal one:

$$\frac{P\overline{V}}{RT} = 1 (\text{assuming ideality of the gas})$$

For real gases, however, this ratio very rarely is equal to one. This ratio is a useful metric for deviation of a gas from ideality, and it appears often enough that we can give this ratio its own definition, Z, the *compressibility factor*:

$$Z = \frac{P\overline{V}}{RT} (\text{Z is unitless})$$

If Z is less than 1, the gas is more compact than we'd predict the corresponding ideal gas to be; if Z is greater than 1, the gas is more spread out than we'd predict the corresponding ideal gas to be. Graphs of compressibilities of gases are some of the first comparison graphs you tend to get exposed to in physical chemistry, and it's worth it to look closely at an example of such a graph and interpret it.

Compressibility factors for nitrogen as a function of pressure and temperature

Compressibility factors as a function of temperature and pressure for nitrogen gas.
Image taken from "Retired Pchem Prof" on Wikimedia Commons; CC BY-SA 4.0.

The most vivid differences in compressibility on this graph for nitrogen are found at a temperature of 220 K. At this comparatively low temperature, nitrogen molecules are able to attract one another more than you'd expect for an ideal gas even when the pressure the gas is under gets relatively high; therefore the gas tends to be more densely packed than ideal, and the compressibility is less than 1. However, when pressure gets high enough (approximately above 230 bar), repulsion between the gas molecules because of their volume takes over, and the gas molecules are more spread out than you would expect an ideal gas to be at that pressure; the compressibility is greater than 1.

At higher temperatures, as you'd expect, there is much less attraction between the gas molecules because the speed at which the molecules are moving don't allow for a great deal of attraction. Once the temperature reaches a certain level, at no point do the gas molecules appear to attract one another into a more dense packing at all; any substantial pressure causes the repulsive effects to have greater significance.

The virial equation is even more elegantly written in terms of the compressibility factor:

$$P\overline{V} = RT\left(1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \frac{D}{\overline{V}^3} + \cdots\right) \rightarrow Z = \frac{P\overline{V}}{RT} = 1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \frac{D}{\overline{V}^3} + \cdots$$

Our tabulation of the second virial coefficient in the last section made note that the values of B depend on temperature. There were certain values of B for low temperatures that were negative, and for high temperatures that were positive. The immediate implication is that there is a temperature where B goes to zero, and (if we continue to ignore the higher terms of the virial expansion as we have been), the compressibility factor reverts back to one:

$$Z = \frac{P\overline{V}}{RT_B} = 1 T_B \rightarrow \text{Boyle temperature}$$

This *Boyle temperature* is unique for every gas. The virial equation doesn't give a whole lot of clarity to what the Boyle temperature actually represents, however, other than a temperature where virial properties magically go to zero.

Making the van der Waals equation fit into the form of the compressibility factor is a bit more of an algebraic challenge, but a worthwhile one to take on. Let's start by taking the van der Waals equation in terms of the molar volume, and solve the equation for pressure:

$$\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT \rightarrow P + \frac{a}{\overline{V}^2} = \frac{RT}{\overline{V} - b} \rightarrow P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

By then multiplying every term by the molar volume divided by RT, we can then build an expression that's equivalent to the compressibility factor:

$$P\frac{\overline{V}}{RT}=\frac{RT}{\overline{V}-b}\frac{\overline{V}}{RT}-\frac{a}{\overline{V}^2}\frac{\overline{V}}{RT}\rightarrow Z=\frac{P\overline{V}}{RT}=\frac{\overline{V}}{\overline{V}-b}-\frac{a}{\overline{V}RT}$$

We have one term in this difference with molar volume isolatable in the denominator; in order to make this equivalent to the virial equation, we need to have the other term set up like this as well. It turns out that the best first step to do this is to transform the first term into a Taylor series expansion. We start by dividing top and bottom of that fraction by the molar volume:

$$\frac{P\overline{V}}{RT}=\frac{\overline{V}/\overline{V}}{\overline{V}/\overline{V}-b/\overline{V}}-\frac{a}{\overline{V}RT}\rightarrow\frac{P\overline{V}}{RT}=\frac{1}{1-b/\overline{V}}-\frac{a}{\overline{V}RT}$$

We now have the first term in the form 1/1-*x*, which can be expanded by the Taylor series into 1 + *x* + x^2 + x^3 + ... Here, *x* is *b* divided by the molar volume:

$$\frac{P\overline{V}}{RT}=1+\frac{b}{\overline{V}}+\left(\frac{b}{\overline{V}}\right)^2+\left(\frac{b}{\overline{V}}\right)^3+\cdots-\frac{a}{\overline{V}RT}$$

Recall the full form of the virial equation that we rederived earlier in the section in terms of the molar volume:

$$\frac{P\overline{V}}{RT}=1+\frac{B}{\overline{V}}+\frac{C}{\overline{V}^2}+\frac{D}{\overline{V}^3}+\cdots$$

We've only provided values for the second virial coefficient *B*; that's because we made the decision that only extending the virial equation to the second term would be sufficient for approximating the real behavior of a gas. For a similar reason, we're going to limit the Taylor series expansion to eliminate terms in the molar volume squared and beyond. The simplified version of the rearranged van der Waals and virial equations, therefore, are these:

$$\frac{P\overline{V}}{RT}=1+\frac{b}{\overline{V}}-\frac{a}{\overline{V}RT}=1+\frac{b-a/RT}{\overline{V}}$$

$$\frac{P\overline{V}}{RT}=1+\frac{B}{\overline{V}}$$

The upshot of all of this rearrangement is that we've expressed the second virial coefficient *B* in terms of the two van der Waals coefficients:

$$B=b-\frac{a}{RT}$$

That's not the only benefit to this derivation. At the Boyle temperature T_B, we achieve ideality in gas behavior; in terms of the virial equation, *B* = 0 at the Boyle temperature. Therefore we can do one more simple rearrangement:

$$0=b-\frac{a}{RT_B}\rightarrow b=\frac{a}{RT_B}\rightarrow T_B=\frac{a}{bR}$$

The van der Waals constants, therefore, contain information about when the gas behaves ideally.

Building these kinds of theoretical connections between relationships is one of the core tasks we pursue in our study of physical chemistry. We can make a great deal of headway with algebraic rearrangement. Ultimately, however, we'll need the tools of the calculus to describe changes in the systems we'll study over time.

1.10: The ideal gas law, functions and derivatives

The ideal gas law gets taught and learned in a easily memorized way:

$$PV = nRT$$

However, when it comes to visualizing the realities of the ideal gas law in graphical form, it's more useful to rearrange the equation. Most presentations of ideal gas behavior as a function of a variable of state make pressure the dependent variable:

$$P(n, T, V) = \frac{nRT}{V}$$

Note that the left side is not merely pressure P, but is pressure as a function of the other three state variables - $P(n, T, V)$. Because this is a function of more than one variable, it resists most of the understanding of calculus we obtain early in our mathematical education, where we only take derivatives of functions of a single variable. Taking derivatives of one variable when other variables are changing isn't often useful for explanation.

So we say this expression has no meaning:

$$\frac{dP}{dT} \rightarrow \text{meaningless}$$

However, let's say we're only interested in the rate of change of pressure as temperature changes, leaving number of moles constant and volume constant (we describe this as change behavior in a closed, rigid container). That *does* have meaning, but we need to express it in a new way, a way we haven't seen before. We describe this as a *partial derivative,* in this case a partial derivative of pressure with respect to temperature, with moles and volume constant. We notate this derivative like this:

$$\left(\frac{\partial P}{\partial T}\right)_{n,V}$$

Using the lower-case Greek letter ∂ is our indicator that this is a *partial* derivative that will focus on only one variable; the variables to be held constant (n, V) are placed in the subscript at lower right. Therefore the partial derivative is equivalent to a derivative of a single variable with all the constants factored out:

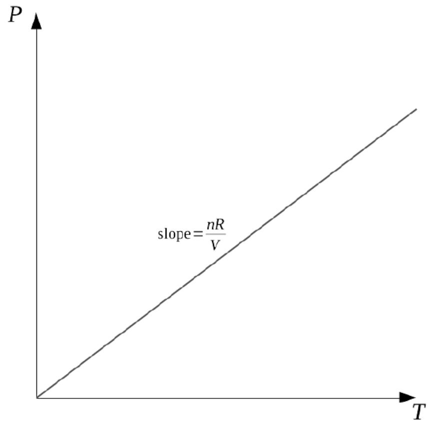
$$\left(\frac{\partial P}{\partial T}\right)_{n,V} = \left(\frac{\partial}{\partial T}\frac{nRT}{V}\right)_{n,V} = \frac{nR}{V}\frac{d}{dT}T$$

But the first derivative with respect to T of T is just 1, and this expression can be easily simplified:

$$\left(\frac{\partial P}{\partial T}\right)_{n,V} = \frac{nR}{V}$$

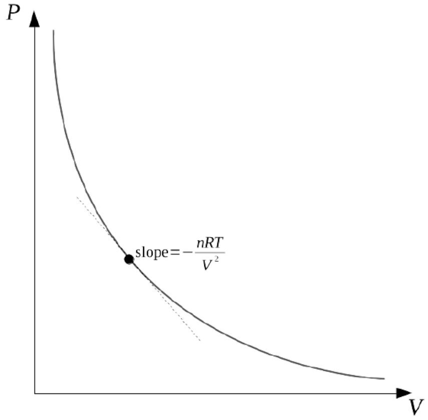
This means that if moles and volume are held constant, the derivative of pressure with respect to temperature must be a constant as well.

This is not surprising!



The relationship between pressure and temperature is a linear relationship, after all; we could just solve the ideal gas law for P/T and we'd get the same slope nR/V. A linear relationship between a dependent and an independent variable is a relationship where the derivative of the dependent variable doesn't change, because the slope of the graph isn't changing.

There are many relationships between the variables of state that turn out to be linear in this way. Not all of them do, however. The most important example of a nonlinear relationship between variables of state is the relationship between pressure and volume:



Just a quick scan of this graph indicates that this *won't* give us a constant slope at every position the way the pressure vs. temperature graph did. And indeed, we run into an additional application of the calculus when we go to take the derivative of a function of pressure with respect to volume, holding temperature and moles constant - the volume is in the denominator, and derivatives of negative powers of a quantity must be negative themselves:

$$\left(\frac{\partial P}{\partial V}\right)_{n,T}=\left(\frac{\partial}{\partial V}\frac{nRT}{V}\right)_{n,T}=nRT\left(\frac{d}{dV}\frac{1}{V}\right)=nRT\left(-\frac{1}{V^2}\right)$$

$$\left(\frac{\partial P}{\partial V}\right)_{n,T}=\left(-\frac{nRT}{V^2}\right)$$

This is a little more involved, but again it's not surprising. At every point, as pressure is increased, volume of the container decreases; the rate of change of pressure with respect to volume is negative. The rate of change is steepest at small values of V and shallowest at large values of V; that reflects the term of V^2 in the denominator of the derivative. The mathematics of the derivative predicts the trend of the graph.

We take derivatives in physical chemistry with this purpose in mind. We are using these derivatives to build our explanatory power for the trends that are fundamental to the relationship between the variables of state.

1.11: Functions of Two Independent Variables

A (real) function of one variable, $y = f(x)$, defines a curve in the plane. The first derivative of a function of one variable can be interpreted graphically as the slope of a tangent line, and dynamically as the rate of change of the function with respect to the variable Figure $1.11.1$.

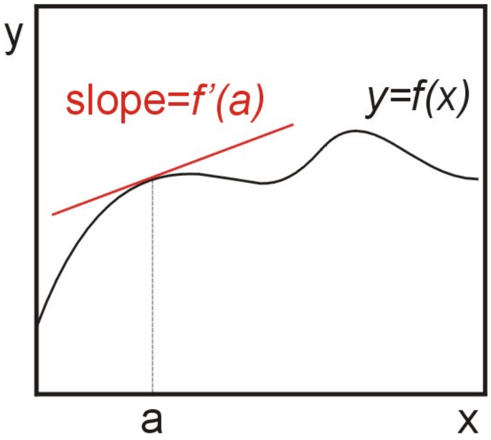


Figure 1.11.1: Geometric interpretation of a derivative. (CC BY-NC-SA; Marcia Levitus)

A function of two independent variables, $z = f(x, y)$, defines a surface in three-dimensional space. For a function of two or more variables, there are as many independent first derivatives as there are independent variables. For example, we can differentiate the function $z = f(x, y)$ with respect to x keeping y constant. This derivative represents the slope of the tangent line shown in Figure $1.11.2A$. We can also take the derivative with respect to y keeping x constant, as shown in Figure $1.11.2B$.

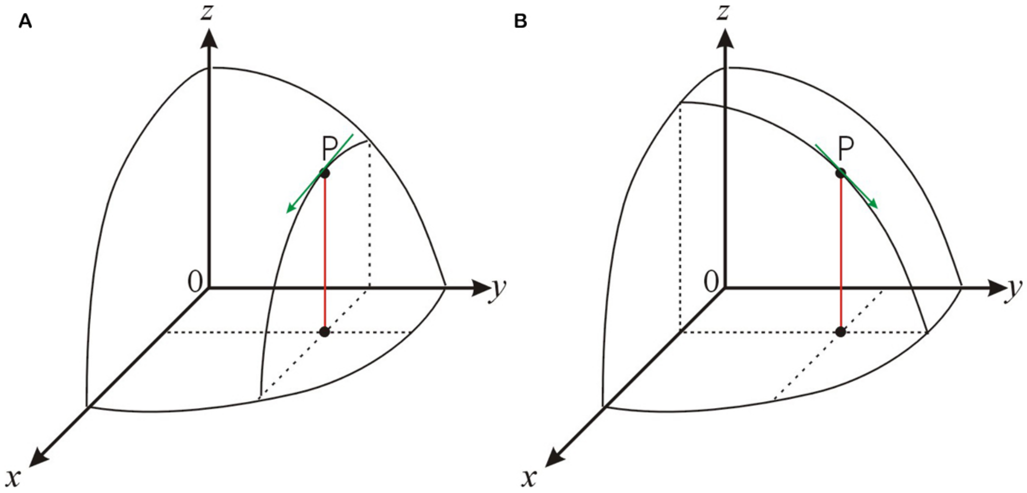


Figure 1.11.2: Geometric interpretation of a partial derivative. (CC BY-NC-SA; Marcia Levitus)

For example, let's consider the function $z = 3x^2 - y^2 + 2xy$. We can take the derivative of this function with respect to x treating y as a constant. The result is $6x + 2y$. This is the partial derivative of the function with respect to x, and it is written:

$$\left(\frac{\partial z}{\partial x}\right)_y = 6x + 2y$$

where the small subscripts indicate which variables are held constant. Analogously, the partial derivate of z with respect to y is:

$$\left(\frac{\partial z}{\partial y}\right)_x = 2x - 2y$$

We can extend these ideas to functions of more than two variables. For example, consider the function $f(x, y, z) = x^2 y/z$. We can differentiate the function with respect to x keeping y and z constant to obtain:

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = 2x\frac{y}{z}$$

We can also differentiate the function with respect to z keeping x and y constant:

$$\left(\frac{\partial f}{\partial z}\right)_{x,y} = -x^2y/z^2$$

and differentiate the function with respect to y keeping x and z constant:

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} = \frac{x^2}{z}$$

Functions of two or more variables can be differentiated partially more than once with respect to either variable while holding the other constant to yield second and higher derivatives. For example, the function $z = 3x^2 - y^2 + 2xy$ can be differentiated with respect to x two times to obtain:

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right)_y = \left(\frac{\partial^2 z}{\partial x^2}\right)_y = 6$$

We can also differentiate with respect to x first and y second:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial^2 f}{\partial y \partial x}\right) = 2$$

> Check the videos below if you are learning this for the first time, or if you feel you need to refresh the concept of partial derivatives.
>
> - Partial derivatives: http://patrickjmt.com/derivatives-finding-partial-derivatives (don't get confused by the different notation!)
> - Partial derivatives: http://www.youtube.com/watch?v=vxJR5graUfI
> - Higher order partial derivatives: http://www.youtube.com/watch?v=3itjTS2Y9oE

If a function of two or more variables and its derivatives are single-valued and continuous, a property normally attributed to physical variables, then the mixed partial second derivatives are equal (Euler reciprocity):

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right) \tag{1.11.1}$$

For example, for $z = 3x^2 - y^2 + 2xy$:

$$\left(\frac{\partial^2 f}{\partial y \partial x}\right) = \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial y}(6x + 2y)\right)_x = 2$$

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial}{\partial x}(-2y + 2x)\right)_y = 2$$

Another useful property of the partial derivatives is the so-called reciprocal identity, which holds when the same variables are held constant in the two derivatives:

$$\left(\frac{\partial y}{\partial x}\right) = \frac{1}{\left(\frac{\partial x}{\partial y}\right)} \tag{1.11.2}$$

For example, for $z = x^2 y$:

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}x^2 y\right)_y = 2xy$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y = \frac{1}{2y}(z/y)^{-1/2} = \frac{1}{2xy} = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

Finally, let’s mention the cycle rule. For a function $z(x,y)$:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \tag{1.11.3}$$

We can construct other versions as follows:

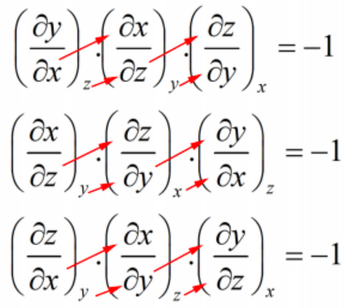


Figure 1.11.3: The chain rule: Start with any partial derivative, and follow the pattern to construct the rest (CC BY-NC-SA; Marcia Levitus)

For example, for $z = x^2 y$:

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial}{\partial x}(z/x^2)\right)_z = -2z/x^3$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y = \frac{1}{2y}(z/y)^{-1/2}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}x^2 y\right)_x = x^2$$

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -\frac{2z}{x^3}\frac{1}{2y}\left(\frac{y}{z}\right)^{1/2} x^2 = -\left(\frac{z}{y}\right)^{1/2}\frac{1}{x} = -\left(\frac{x^2 y}{y}\right)^{1/2}\frac{1}{x} = -1$$

Before discussing partial derivatives any further, let’s introduce a few physicochemical concepts to put our discussion in context.

1.12: The Equation of State

Note

From the last section, the cycle rule is defined as follows:

$$\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x=-1 \tag{1.12.1}$$

The thermodynamic state of a system, such as a fluid, is defined by specifying a set of measurable properties sufficient so that all remaining properties are determined. For example, if you have a container full of a gas, you may specify the pressure, temperature and number of moles, and this should be sufficient for you to calculate other properties such as the density and the volume. In other words, the temperature (T), number of moles (n), volume (V) and pressure (P) are not all independent variables.

Ideal Gas Equation of State

To make sense of this statement, let’s consider an ideal gas. You know from your introductory chemistry courses[1] that temperature, number of moles, volume and pressure are related through a universal constant R:

$$P=\frac{nRT}{V} \tag{1.12.2}$$

If P is expressed in atmospheres, V in liters, and T in Kelvin, then $R=0.082\ \frac{L\times atm}{K\times mol}$

This expression tells you that the four variables cannot be changed independently. If you know three of them, you also know the fourth.

Equation 1.12.2 is one particular case of what is known as an **equation of state**. An equation of state is an expression relating the density of a fluid with its temperature and pressure. Note that the density is related to the number of moles and the volume, so it takes care of these two variables together. There is no single equation of state that predicts the behavior of all substances under all conditions. Equation 1.12.2, for example, is a good approximation for non polar gases at low densities (low pressures and high temperatures). Other more sophisticated equations are better suited to describe other systems in other conditions, but there is no universal equation of state.

In general, for a simple fluid, an equation of state will be a relationship between P and the variables T, V and n:

$$P=P(T,V,n)=P(T,V_m),$$

where V_m is the molar volume, V/n. The molar volume is sometimes written as $\bar{V}$. For example, Equation 1.12.2 can be rerwritten as

$$P=\frac{RT}{\bar{V}}.$$

Let’s ‘play’ with the equation of state for an ideal gas. The partial derivative $\left(\frac{\partial P}{\partial T}\right)_{V,n}$ represents how the pressure changes as we change the temperature of the container at constant volume and constant n:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n}=\frac{nR}{V}$$

It is a relief that the derivative is positive, because we know that an increase in temperature causes an increase in pressure! This also tells us that if we increase the temperature by a small amount, the increase in pressure will be larger in a small container than in a large container.

The partial derivative $\left(\frac{\partial P}{\partial V}\right)_{T,n}$ represents how the pressure changes as we change the volume of the container at constant temperature and constant n:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}=-\frac{nRT}{V^2}$$

Again, we are happy to see the derivative is negative. If we increase the volume we should see a decrease in pressure as long as the temperature is held constant. This is not too different from squeezing a balloon (don't try this at home!).

We can also write an equation that represents how the volume changes with a change in pressure: $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. From Equation 1.12.2,

$$V=\frac{nRT}{P}$$

and therefore:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n}=-\frac{nRT}{P^2}$$

Let's compare these two derivatives:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n}=-\frac{nRT}{P^2}=-\frac{nRT}{(nRT/V)^2}=-\frac{V^2}{nRT}=\frac{1}{\left(\frac{\partial P}{\partial V}\right)_{T,n}}$$

Surprised? You shouldn't be based on the inverse rule! (Equation ???). Note that this works because we hold the same variables constant in both cases.

Now, you may argue that the inverse rule is not particularly useful because it doesn't take a lot of work to solve for V and perform $\left(\frac{\partial V}{\partial P}\right)_{T,n}$.

Dieterici's Equation of State

Let's consider a more complex equation of state known as Dieterici's equation of state for a real gas:

$$P=\frac{RT}{\bar{V}-b}e^{-a/(R\bar{V}T)}$$

Here, a and b are constants that depend on the particular gas (e.g. whether we are considering H_2 or CO_2). Let's say you are asked to obtain $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. What do you do? Do you find the inverse rule useful now?

Let's go back to the ideal gas, and calculate other partial derivatives:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}=-\frac{nRT}{V^2} \tag{1.12.3}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n}=\frac{nR}{P} \tag{1.12.4}$$

$$\left(\frac{\partial T}{\partial P}\right)_{V,n}=\frac{V}{nR} \tag{1.12.5}$$

Let's calculate the product:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}\left(\frac{\partial T}{\partial P}\right)_{V,n}=-\frac{nRT}{V^2}\frac{nR}{P}\frac{V}{nR}=-\frac{nRT}{VP}=-1$$

In the last step, we used Equation 1.12.2. Surprised? You shouldn't be based on the cycle rule! (Equation 1.12.1). Again, this is not particularly useful for an ideal gas, but let's think about Dieterici's equation again and let's assume that you are interested in calculating $\left(\frac{\partial V}{\partial T}\right)_{P,n}$. What would you do?

1.13: Compressibility and Expansivity

Isothermal Compressibility (κ_T)

A very important property of a substance is how compressible it is. Gases are very compressible, so when subjected to high pressures, their volumes decrease significantly (think Boyle's Law!) Solids and liquids however are not as compressible. However, they are not entirely incompressible! High pressure will lead to a decrease in volume, even if it is only slight. And, of course, different substances are more compressible than others.

To quantify just how compressible substances are, it is necessary to define the property. The **isothermal compressibility** is defined by the fractional differential change in volume due to a change in pressure.

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{1.13.1}$$

The negative sign is important in order to keep the value of κ_T positive, since an increase in pressure will lead to a decrease in volume. The $1/V$ term is needed to make the property intensive so that it can be tabulated in a useful manner.

Isobaric Thermal Expansivity (α)

Another very important property of a substance is how its volume will respond to changes in temperature. Again, gases respond profoundly to changes in temperature (think Charles' Law!) whereas solids and liquid will have more modest (but not negligible) responses to changes in temperature. (For example, If mercury or alcohol didn't expand with increasing temperature, we wouldn't be able to use those substances in thermometers.)

The definition of the **isobaric thermal expansivity** (or sometimes called the expansion coefficient) is

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{1.13.2}$$

As was the case with the compressibility factor, the $1/V$ term is needed to make the property intensive, and thus able to be tabulated in a useful fashion. In the case of expansion, volume tends to increase with increasing temperature, so the partial derivative is positive.

Deriving an Expression for a Partial Derivative (Type I): The reciprocal rule

Consider a system that is described by three variables, and for which one can write a mathematical constraint on the variables

$$F(x,y,z)=0$$

Under these circumstances, one can specify the state of the system varying only two parameters independently because the third parameter will have a fixed value. As such one could define two functions: $z(x,y)$ and $y(x,z)$.

This allows one to write the total differentials for dz and dy as follows

$$dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy \tag{1.13.3}$$

and

$$dy=\left(\frac{\partial y}{\partial x}\right)_z dx+\left(\frac{\partial y}{\partial z}\right)_x dz \tag{1.13.4}$$

Substituting the Equation 1.13.4expression into Equation 1.13.3:

$$\begin{aligned} dz &=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial x}\right)_z dx+\left(\frac{\partial y}{\partial z}\right)_x dz\right] && (1.13.5)\\ &=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_z dx+\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial z}\right)_x dz && (1.13.6)\end{aligned}$$

If the system undergoes a change following a pathway where x is held constant ($dx = 0$), this expression simplifies to

$$dz = \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

And so for changes for which $dz \neq 0$,

$$\left(\frac{\partial z}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

This *reciprocal rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straightforward, albeit less rigorous, manner. Begin by writing the total differential for $z(x, y)$ (Equation 1.13.3):

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dz and constrain to constant x.

$$\left.\frac{dz}{dz}\right|_x = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dz}\right|_x + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dz}\right|_x \tag{1.13.7}$$

Noting that

$$\left.\frac{dz}{dz}\right|_x = 1$$

$$\left.\frac{dx}{dz}\right|_x = 0$$

and

$$\left.\frac{dy}{dz}\right|_x = \left(\frac{\partial y}{\partial z}\right)_x$$

Equation 1.13.7becomes

$$1 = \left(\frac{\partial z}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x$$

or

$$\left(\frac{\partial z}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

This "formal" method of partial derivative manipulation is convenient and useful, although it is not mathematically rigorous. However, it does work for the kind of partial derivatives encountered in thermodynamics because the variables are **state variables** and the differentials are **exact**.

Deriving an Expression for a Partial Derivative (Type II): The Cyclic Permutation Rule

This alternative derivation follow the initial steps in the derivation above to Equation 1.13.6:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

If the system undergoes a change following a pathway where z is held constant ($dz = 0$), this expression simplifies to

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dy + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx$$

And so for and changes in which $dx \neq 0$

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This *cyclic permutation rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straight-forward, albeit less rigorous, manner. As with the derivation above, we wegin by writing the total differential of $z(x,y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dx and constrain to constant z.

$$\left.\frac{dz}{dx}\right|_z = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dx}\right|_z + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dx}\right|_z \tag{1.13.8}$$

Note that

$$\left.\frac{dz}{dx}\right|_z = 0$$

$$\left.\frac{dx}{dx}\right|_z = 1$$

and

$$\left.\frac{dy}{dx}\right|_z = \left(\frac{\partial y}{\partial x}\right)_z$$

Equation 1.13.8 becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

which is easily rearranged to

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This type of transformation is very convenient, and will be used often in the manipulation of partial derivatives in thermodynamics.

✓ Example 1.13.1: Expanding Thermodynamic Functions

Derive an expression for

$$\frac{\alpha}{\kappa_T}. \tag{1.13.9}$$

in terms of derivatives of thermodynamic functions using the definitions in Equations 1.13.1 and 1.13.2.

Solution

Substituting Equations 1.13.1 and 1.13.2 into the Equation 1.13.9

$$\frac{\alpha}{\kappa_T} = \frac{\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p}{-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T}$$

Simplifying (canceling the $1/V$ terms and using transformation Type I to invert the partial derivative in the denominator) yields

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

Applying Transformation Type II give the final result:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T}\right)_V$$

1.14: The Total Differential

In Chapter 8 we learned that partial derivatives indicate how the dependent variable changes with one particular independent variable keeping the others fixed. In the context of an equation of state $P = P(T, V, n)$, the partial derivative of P with respect to V at constant T and n is:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

and physically represents how the pressure varies as we change the volume at constant temperature and constant n.

The partial derivative of P with respect to T at constant V and n is:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n}$$

and physically represents how the pressure varies as we change the temperature at constant volume and constant n.

What happens with the dependent variable (in this case P) if we change two or more independent variables simultaneously? For an infinitesimal change in volume and temperature, we can write the change in pressure as:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \tag{1.14.1}$$

Equation 1.14.1 is called the *total differential of* P, and it simply states that the change in P is the sum of the individual contributions due to the change in V at constant T and the change in T at constant V. This equation is true for infinitesimal changes. If the changes are not infinitesimal we will integrate this expression to calculate the change in P.[differentials_position1]

Let's now consider the volume of a fluid, which is a function of pressure, temperature and the number of moles: $V = V(n, T, P)$. The total differential of V, by definition, is:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,V} dn \tag{1.14.2}$$

If we want to calculate the change in volume in a fluid upon small changes in P, T and n, we could use:

$$\Delta V \approx \left(\frac{\partial V}{\partial T}\right)_{P,n} \Delta T + \left(\frac{\partial V}{\partial P}\right)_{T,n} \Delta P + \left(\frac{\partial V}{\partial n}\right)_{T,V} \Delta n \tag{1.14.3}$$

Of course, if we know the function $V = V(n, T, P)$, we could also calculate ΔV as $V_f - F_i$, where the final and initial volumes are calculated using the final and initial values of P, T and n. This seems easy, so why do we need to bother with Equation 1.14.3? The reason is that sometimes we can measure the partial derivatives experimentally, but we do not have an equation of the type $V = V(n, T, P)$ to use. For example, the following quantities are accessible experimentally and tabulated for different fluids and materials (Fig. [fig:diff_tables]):

- $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}$ (coefficient of thermal expansion)
- $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{V,n}$ (isothermal compressibility)[differentials:compressibility]
- $V_m = \left(\frac{\partial V}{\partial n}\right)_{P,T}$ (molar volume)

Using these definitions, Equation 1.14.2 becomes:

$$dV = \alpha V dT - \kappa V dP + V_m dn \tag{1.14.4}$$

You can find tables with experimentally determined values of α and κ under different conditions, which you can use to calculate the changes in V. Again, as we will see later in this chapter, this equation will need to be integrated if the changes are not small. In any case, the point is that you may have access to information about the derivatives of the function, but not to the function itself (in this case V as a function of T, P, n).

In general, for a function $u = u(x_1, x_2 \ldots x_n)$, we define the total differential of u as:

$$du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2 \ldots x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 \ldots x_n} dx_2 + \ldots + \left(\frac{\partial u}{\partial x_n}\right)_{x_1 \ldots x_{n-1}} dx_n \tag{1.14.5}$$

Example 1.14.1

Calculate the total differential of the function $z = 3x^3 + 3yx^2 + xy^2$.

Solution

By definition, the total differential is:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

For the function given in the problem,

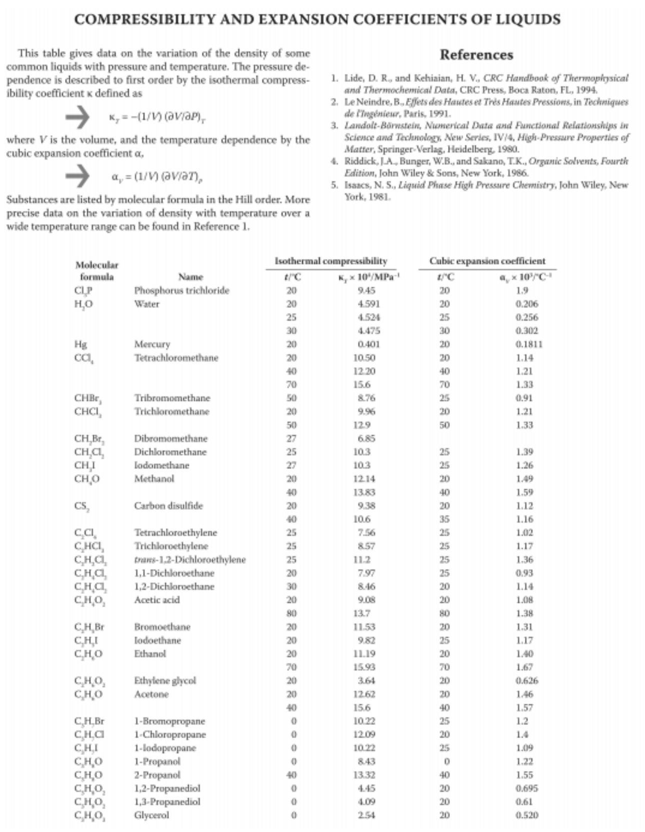
$$\left(\frac{\partial z}{\partial x}\right)_y = 9x^2 + 6xy + y^2$$

and

$$\left(\frac{\partial z}{\partial y}\right)_x = 3x^2 + 2xy$$

and therefore,

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$



COMPRESSIBILITY AND EXPANSION COEFFICIENTS OF LIQUIDS

This table gives data on the variation of the density of some common liquids with pressure and temperature. The pressure dependence is described to first order by the isothermal compressibility coefficient κ defined as

$$\kappa_T = -(1/V)\,(\partial V/\partial P)_T$$

where V is the volume, and the temperature dependence by the cubic expansion coefficient α,

$$\alpha_V = (1/V)\,(\partial V/\partial T)_P$$

Substances are listed by molecular formula in the Hill order. More precise data on the variation of density with temperature over a wide temperature range can be found in Reference 1.

References

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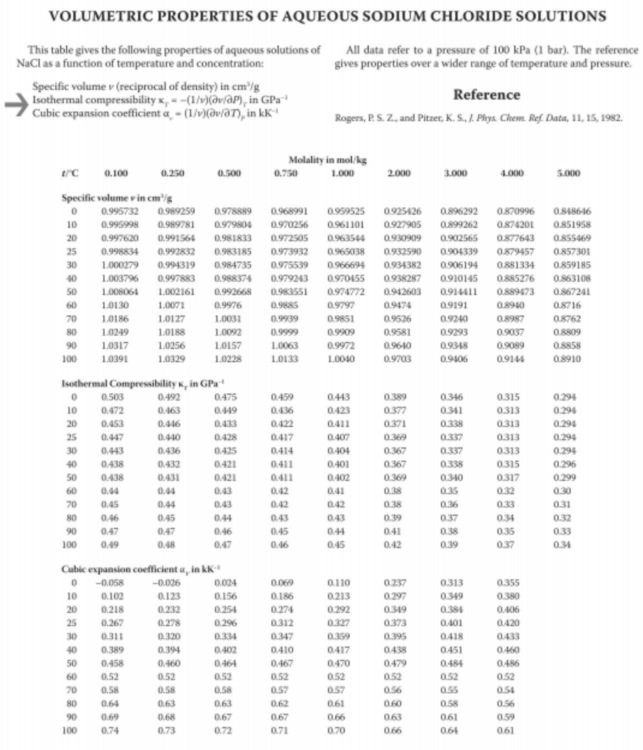
4. Riddick, J.A., Bunger, W.B., and Sakano, T.K., *Organic Solvents, Fourth Edition*, John Wiley & Sons, New York, 1986.
5. Isaacs, N. S., *Liquid Phase High Pressure Chemistry*, John Wiley, New York, 1981.

Molecular formula	Name	Isothermal compressibility		Cubic expansion coefficient	
		t/°C	$\kappa_T \times 10^4$/MPa^{-1}	t/°C	$\alpha_V \times 10^3$/°C^{-1}
Cl_3P	Phosphorus trichloride	20	9.45	20	1.9
H_2O	Water	20	4.591	20	0.206
		25	4.524	25	0.256
		30	4.475	30	0.302
Hg	Mercury	20	0.401	20	0.1811
CCl_4	Tetrachloromethane	20	10.50	20	1.14
		40	12.20	40	1.21
		70	15.6	70	1.33
$CHBr_3$	Tribromomethane	50	8.76	25	0.91
$CHCl_3$	Trichloromethane	20	9.96	20	1.21
		50	12.9	50	1.33
CH_2Br_2	Dibromomethane	27	6.85		
CH_2Cl_2	Dichloromethane	25	10.3	25	1.39
CH_3I	Iodomethane	27	10.3	25	1.26
CH_4O	Methanol	20	12.14	20	1.49
		40	13.83	40	1.59
CS_2	Carbon disulfide	20	9.38	20	1.12
		40	10.6	35	1.16
C_2Cl_4	Tetrachloroethylene	25	7.56	25	1.02
C_2HCl_3	Trichloroethylene	25	8.57	25	1.17
$C_2H_2Cl_2$	*trans*-1,2-Dichloroethylene	25	11.2	25	1.36
$C_2H_4Cl_2$	1,1-Dichloroethane	20	7.97	25	0.93
$C_2H_4Cl_2$	1,2-Dichloroethane	30	8.46	20	1.14
$C_2H_4O_2$	Acetic acid	20	9.08	20	1.08
		80	13.7	80	1.38
C_2H_5Br	Bromoethane	20	11.53	20	1.31
C_2H_5I	Iodoethane	20	9.82	25	1.17
C_2H_6O	Ethanol	20	11.19	20	1.40
		70	15.93	70	1.67
$C_2H_6O_2$	Ethylene glycol	20	3.64	20	0.626
C_3H_6O	Acetone	20	12.62	20	1.46
		40	15.6	40	1.57
C_3H_7Br	1-Bromopropane	0	10.22	25	1.2
C_3H_7Cl	1-Chloropropane	0	12.09	20	1.4
C_3H_7I	1-Iodopropane	0	10.22	25	1.09
C_3H_8O	1-Propanol	0	8.43	0	1.22
C_3H_8O	2-Propanol	40	13.32	40	1.55
$C_3H_8O_2$	1,2-Propanediol	0	4.45	20	0.695
$C_3H_8O_2$	1,3-Propanediol	0	4.09	20	0.61
$C_3H_8O_3$	Glycerol	0	2.54	20	0.520



VOLUMETRIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

This table gives the following properties of aqueous solutions of NaCl as a function of temperature and concentration:

Specific volume v (reciprocal of density) in cm^3/g
Isothermal compressibility $\kappa_T = -(1/v)(\partial v/\partial P)_T$ in GPa^{-1}
Cubic expansion coefficient $\alpha_v = (1/v)(\partial v/\partial T)_p$ in kK^{-1}

All data refer to a pressure of 100 kPa (1 bar). The reference gives properties over a wider range of temperature and pressure.

Reference

Rogers, P. S. Z., and Pitzer, K. S., *J. Phys. Chem. Ref. Data*, 11, 15, 1982.

	Molality in mol/kg								
t/°C	**0.100**	**0.250**	**0.500**	**0.750**	**1.000**	**2.000**	**3.000**	**4.000**	**5.000**
Specific volume v in cm^3/g									
0	0.995732	0.989259	0.978889	0.968991	0.959525	0.925426	0.896292	0.870996	0.848646
10	0.995998	0.989781	0.979804	0.970256	0.961101	0.927905	0.899262	0.874201	0.851958
20	0.997620	0.991564	0.981833	0.972505	0.963544	0.930909	0.902565	0.877643	0.855469
25	0.998834	0.992832	0.983185	0.973932	0.965038	0.932590	0.904339	0.879457	0.857301
30	1.000279	0.994319	0.984735	0.975539	0.966694	0.934382	0.906194	0.881334	0.859185
40	1.003796	0.997883	0.988374	0.979243	0.970455	0.938287	0.910145	0.885276	0.863108
50	1.008064	1.002161	0.992668	0.983551	0.974772	0.942603	0.914411	0.889473	0.867241
60	1.0130	1.0071	0.9976	0.9885	0.9797	0.9474	0.9191	0.8940	0.8716
70	1.0186	1.0127	1.0031	0.9939	0.9851	0.9526	0.9240	0.8987	0.8762
80	1.0249	1.0188	1.0092	0.9999	0.9909	0.9581	0.9293	0.9037	0.8809
90	1.0317	1.0256	1.0157	1.0063	0.9972	0.9640	0.9348	0.9089	0.8858
100	1.0391	1.0329	1.0228	1.0133	1.0040	0.9703	0.9406	0.9144	0.8910
Isothermal Compressibility κ_T in GPa^{-1}									
0	0.503	0.492	0.475	0.459	0.443	0.389	0.346	0.315	0.294
10	0.472	0.463	0.449	0.436	0.423	0.377	0.341	0.313	0.294
20	0.453	0.446	0.433	0.422	0.411	0.371	0.338	0.313	0.294
25	0.447	0.440	0.428	0.417	0.407	0.369	0.337	0.313	0.294
30	0.443	0.436	0.425	0.414	0.404	0.367	0.337	0.313	0.294
40	0.438	0.432	0.421	0.411	0.401	0.367	0.338	0.315	0.296
50	0.438	0.431	0.421	0.411	0.402	0.369	0.340	0.317	0.299
60	0.44	0.44	0.43	0.42	0.41	0.38	0.35	0.32	0.30
70	0.45	0.44	0.43	0.42	0.42	0.38	0.36	0.33	0.31
80	0.46	0.45	0.44	0.43	0.43	0.39	0.37	0.34	0.32
90	0.47	0.47	0.46	0.45	0.44	0.41	0.38	0.35	0.33
100	0.49	0.48	0.47	0.46	0.45	0.42	0.39	0.37	0.34
Cubic expansion coefficient α_V in kK^{-1}									
0	−0.058	−0.026	0.024	0.069	0.110	0.237	0.313	0.355	
10	0.102	0.123	0.156	0.186	0.213	0.297	0.349	0.380	
20	0.218	0.232	0.254	0.274	0.292	0.349	0.384	0.406	
25	0.267	0.278	0.296	0.312	0.327	0.373	0.401	0.420	
30	0.311	0.320	0.334	0.347	0.359	0.395	0.418	0.433	
40	0.389	0.394	0.402	0.410	0.417	0.438	0.451	0.460	
50	0.458	0.460	0.464	0.467	0.470	0.479	0.484	0.486	
60	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	
70	0.58	0.58	0.58	0.57	0.57	0.56	0.55	0.54	
80	0.64	0.63	0.63	0.62	0.61	0.60	0.58	0.56	
90	0.69	0.68	0.67	0.67	0.66	0.63	0.61	0.59	
100	0.74	0.73	0.72	0.71	0.70	0.66	0.64	0.61	

Figure 1.14.1: Tables of isothermal compressibilities and expansion coefficients of different fluids (top) and sodium chloride solutions (bottom). Source: CRC Handbook of Physics and Chemistry (CC BY-NC-SA; Marcia Levitus)

Want to see more examples?

- Example 1: http://www.youtube.com/watch?v=z0TxZ0EHzIg Notice that she calls it ’the differential’, but I prefer ’the total differential’.

1.15: Exact and Inexact Differentials

So far, we discussed how to calculate the total differential of a function. If you are given a function of more than one variable, you can calculate its total differential using the definition of a total differential of a function u: ($du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2 \ldots x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 \ldots x_n} dx_2 + \ldots + \left(\frac{\partial u}{\partial x_n}\right)_{x_1 \ldots x_{n-1}} dx_n$). You will have one term for each independent variable. What if we are given a differential (e.g.

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

see Example 9.1) and we are asked to calculate the function whose total differential is dz? This is basically working Example 9.1 backwards: we know the differential, and we are looking for the function. Things are a little bit more complicated than this, because not all differentials are the total differentials of a function. For example, from the example above we know that

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

is the total differential of

$$z(x, y) = 3x^3 + 3yx^2 + xy^2.$$

However, the differential $dz = xydx + x^2dy$ is **not** the total differential of any function $z(x, y)$. You can write down every single function $z(x, y)$ in this planet, calculate their total differentials, and you will never see $dz = xydx + x^2dy$ in your list.

Therefore, the question we are addressing is the following: given a differential, 1) is it the total differential of any function? 2) if it is, which function?

To illustrate the question, let’s say we are given the differential below (notice that I switched to P, V, and T, which are variables you will encounter often in thermodynamics):

$$dP = \frac{RT}{V-b}dT + \left[\frac{RT}{(V-b)^2} - \frac{a}{TV^2}\right]dV \tag{1.15.1}$$

The question is whether this is the total differential of a function $P = P(T, V)$ (we are told that a and b are constants, and we already know that R is a constant). By definition of total differential, if the function exists, its total differential will be:

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \tag{1.15.2}$$

Comparing Equation 1.15.1 and 1.15.2, if the function exists, its derivatives will have to be:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b} \tag{1.15.3}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{RT}{(V-b)^2} - \frac{a}{TV^2}\right] \tag{1.15.4}$$

If we find a function $P = P(T, V)$ that satisfies these equations at the same time, we know that Equation 1.15.1 will be its total differential.

From Equation 1.15.3, we can calculate P by integrating with respect to T at constant V:

$$\int dP = \int \frac{RT}{V-b}dT \rightarrow P = \frac{R}{V-b}\frac{T^2}{2} + f(V) \tag{1.15.5}$$

where we included an integration constant ($f(V)$) that can be any function of V (we are integrating at constant V).

In order to get an expression for $P(T, V)$, we need to find out $f(V)$ so we can complete the right side of Equation 1.15.5. To do that, we are going to take the derivative of P (Equation 1.15.5 with respect to V, and compare with Equation 1.15.4:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT^2}{2(V-b)^2} + \frac{df(V)}{dV} \tag{1.15.6}$$

Looking at Equation 1.15.4 and 1.15.6, we see that the two expressions do not match, regardless of which function we chose for $f(V)$. This means that Equation 1.15.1 does not represent the total differential of any function $P(V,T)$. We call these differentials **inexact differentials**. If a differential is the total differential of a function, we will call the differential **exact**.

What we did so far is correct, but it is not the easiest way to test whether a differential is exact or inexact. There is, in fact, a very easy way to test for exactness. We'll derive the procedure below, but in the future we can use it without deriving it each time.

Given the differential $dz = f_1(x,y)dx + f_2(x,y)dy$, the differential is exact if

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y \tag{1.15.7}$$

If Equation 1.15.7 does not hold, the differential is inexact. For instance, if $dz = (9x^2+6xy+y^2)dx + (3x^2+2xy)dy$, the functions f_1 and f_2 are $f_1 = 9x^2+6xy+y^2$ and $f_2 = 3x^2+2xy$. To test this differential, we perform the partial derivatives

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = 6x+2y$$

and

$$\left(\frac{\partial f_2(x,y)}{\partial x}\right)_y = 6x+2y$$

The two derivatives are the same, and therefore the differential is said to be exact.

Let's prove why the test of Equation 1.15.7 works. Let's consider a differential of the form $dz = f_1(x,y)dx + f_2(x,y)dy$. If the differential is exact, it is the total differential of a function $z(x,y)$, and therefore:

$$dz = f_1(x,y)dx + f_2(x,y)dy = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{1.15.8}$$

We know that the mixed partial derivatives of a function are independent of the order they are computed:

$$\left(\frac{\partial^2 z}{\partial y \partial x}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

From Equation 1.15.8,

$$f_1(x,y) = \left(\frac{\partial z}{\partial x}\right)_y \rightarrow \left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

$$f_2(x,y) = \left(\frac{\partial z}{\partial y}\right)_x \rightarrow \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

Because the mixed partial derivatives are the same, for an exact differential:

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y$$

This equation is true only for an exact differential because we derived it by assuming that the function $z = z(x,y)$ exists, so its mixed partial derivatives are the same. We can use this relationship to test whether a differential is exact or inexact. If the equality of Equation 1.15.7 holds, the differential is exact. If it does not hold, it is inexact.

✓ Example 1.15.1

Test whether the following differential is exact or inexact:

$$dz = \frac{1}{x^2}dx - \frac{y}{x^3}dy$$

Solution

To test whether dz is exact or inexact, we compare the following derivatives

$$\left(\frac{\partial(1/x^2)}{\partial y}\right)_x \overset{?}{=} \left(\frac{\partial(y/x^3)}{\partial x}\right)_y$$

$$\left(\frac{\partial(1/x^2)}{\partial y}\right)_x = 0$$

$$\left(\frac{\partial(y/x^3)}{\partial x}\right)_y = -3yx^{-4}$$

We conclude that dz is inexact, and therefore there is no function $z(x,y)$ whose total differential is dz.

✓ Example 1.15.2

Determine whether the following differential is exact or inexact. If it is exact, determine $z=z(x,y)$.

$$dz=(2x+y)dx+(x+y)dy$$

Solution

To test whether dz is exact or inexact, we compare the following derivatives

$$\left(\frac{\partial(2x+y)}{\partial y}\right)_x \overset{?}{=} \left(\frac{\partial(x+y)}{\partial x}\right)_y$$

If this equality holds, the differential is exact.

$$\left(\frac{\partial(2x+y)}{\partial y}\right)_x = 1$$

$$\left(\frac{\partial(x+y)}{\partial x}\right)_y = 1$$

Therefore, the differential is exact. Because it is exact, it is the total differential of a function $z(x,y)$. The total differential of $z(x,y)$ is, by definition,

$$dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy$$

Comparing this expression to the differential $dz=(2x+y)dx+(x+y)dy$:

$$\left(\frac{\partial z}{\partial x}\right)_y = (2x+y)$$

$$\left(\frac{\partial z}{\partial y}\right)_x = (x+y) \tag{1.15.9}$$

To find $z(x,y)$, we can integrate the first expression partially with respect to x keeping y constant:

$$\int dz = z = \int (2x+y)dx = x^2+xy+f(y)$$

So far we have

$$z=x^2+xy+f(y) \tag{1.15.10}$$

so we need to find the function $f(y)$ to complete the expression above and finish the problem. To do that, we'll take the derivative of z with respect to y, and compare with Equation 1.15.9. The derivative of Equation 1.15.10is:

$$\left(\frac{\partial z}{\partial y}\right)_x = x+\frac{df(y)}{dy}$$

comparing with Equation 1.15.9we notice that $\frac{df(y)}{dy}=y$, and integrating, we obtain $f(x)=y^2/2+c$

Therefore, $dz=(2x+y)dx+(x+y)dy$ is the total differential of $z=x^2+xy+y^2/2+c$.

We can check our result by working the problem in the opposite direction. If we are given $z=x^2+xy+y^2/2+c$ and we are asked to calculate its total differential, we would apply the definition:

$$dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy$$

and because

$$\left(\frac{\partial z}{\partial x}\right)_y=y+2x$$

and

$$+\left(\frac{\partial z}{\partial y}\right)_x=y+x$$

we would write $dz=(2x+y)dx+(x+y)dy$, which is the differential we were given in the problem.

Check two extra solved examples in this video: http://tinyurl.com/kq4qecu

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CHAPTER OVERVIEW

2: Work, Heat, and the First Law

2.1: Overview of Classical Thermodynamics

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

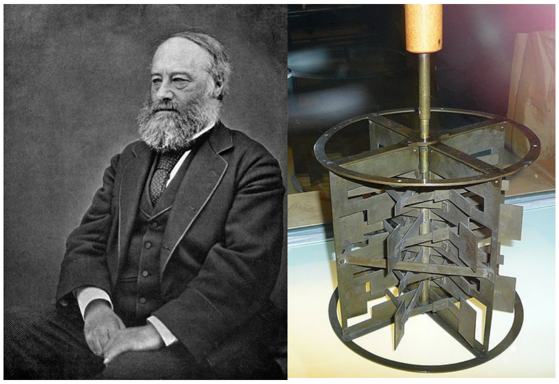


Figure $2.1.1$: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

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

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

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

$$\Delta U = U_f - U_i \tag{2.1.1}$$

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

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

$$\Delta U = q + w$$

or

$$dU = dq + dw$$

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

2.1.1: Heat

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

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

$$dq = C\,dT$$

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

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

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

✓ Example 2.1.1: Heat required to Raise Temperature

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

Solution

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

What is a partial derivative?

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

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

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

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

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

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

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

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

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{2.1.2}$$

and

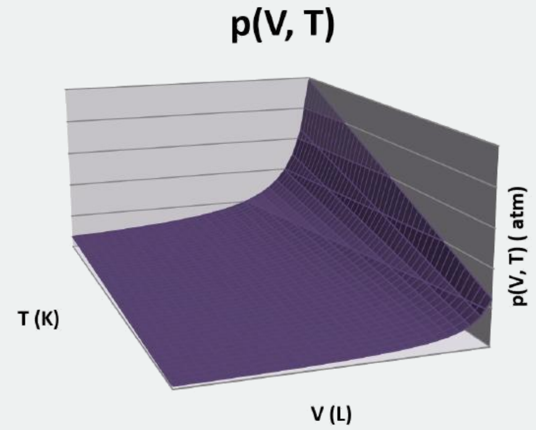
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{2.1.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{2.1.4}$$

or by substituting Equations 2.1.2 and 2.1.3

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



Macroscopic changes can be expressed by integrating the individual pieces of Equation 2.1.4 over appropriate intervals.

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

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

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

or

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

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

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

or

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

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

2.1.2: Work

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

Table 3.1.1: Changes to the System

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

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

✓ Example 2.1.2: Work from a Gas Expansion

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

Solution

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

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

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

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

2.2: Pressure-Volume Work

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

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

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

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

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

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

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

Pressure-volume (PV) work

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

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

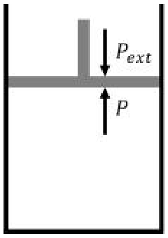


Figure 19.2.1 : A piston with internal pressure P and external pressure P_{ext}.

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

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\,ds) = \int P\,dV \tag{2.2.1}$$

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

Sign Conventions

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

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

To comply with this convention we need to rewrite volume work (Equation 2.2.1) as

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

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

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

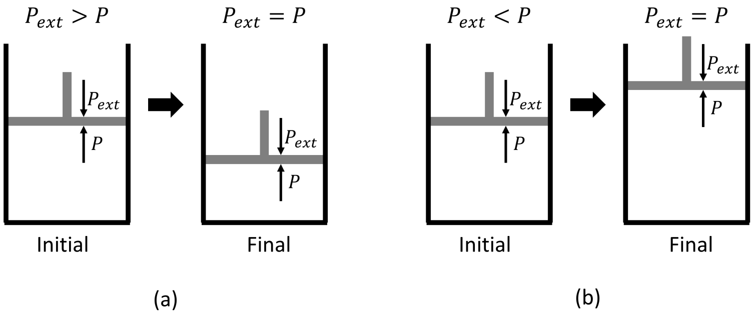


Figure 19.2.2 : Pistons showing a compression (left) and an expansion (right).

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

$$w = -P_{\text{ext}} \int_{V_{initial}}^{V_{final}} dV = -P_{\text{ext}} \Delta V \tag{2.2.2}$$

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

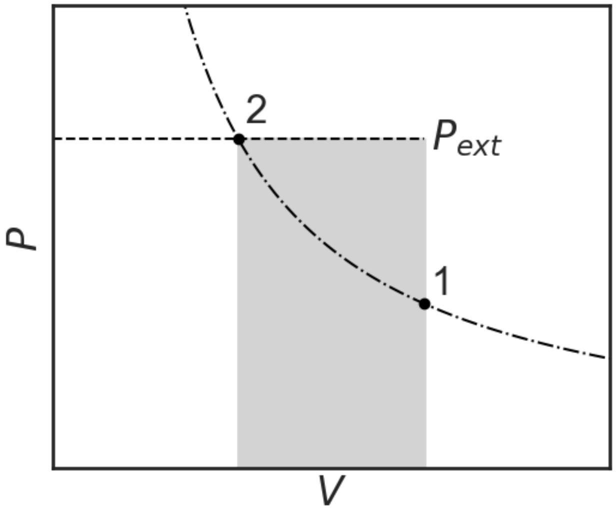


Figure 19.2.3 : A system is compressed under constant external pressure, P_{ext}, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible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

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

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

2.3: Work and Heat are not State Functions

2.3.1: Heat and work are path functions

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

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

Path Functons

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

2.3.2: Reversible versus irreversible

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

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

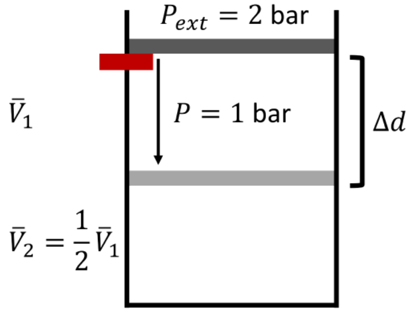


Figure 19.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

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

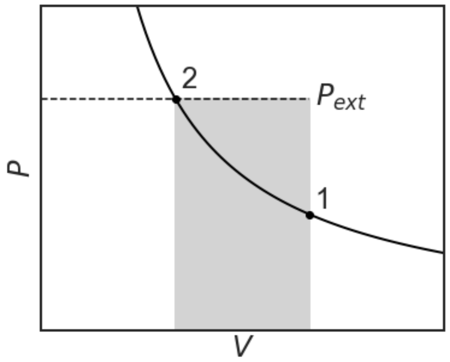


Figure 19.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

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

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

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

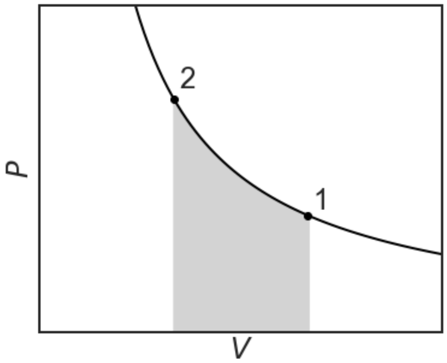


Figure 19.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

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

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

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

Reversible vs. Irreversible Processes

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

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

2.3.2.1: Isothermal Expansion

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

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

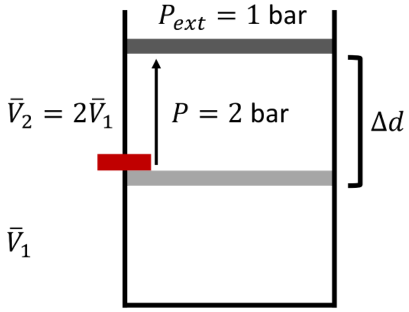


Figure 19.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

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

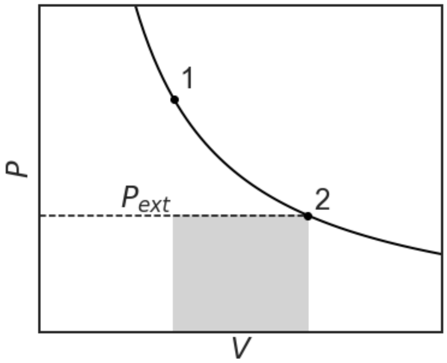


Figure 19.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

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

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

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

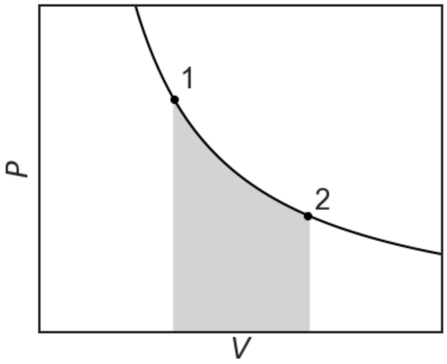


Figure 19.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

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

2.1: Thermodynamic Systems

A thermodynamic system—or just simply a system—is a portion of space with defined boundaries that separate it from its surroundings (see also the title picture of this book). The surroundings may include other thermodynamic systems or physical systems that are not thermodynamic systems. A boundary may be a real physical barrier or a purely notional one. Typical examples of systems are reported in Figure $2.1.1$ below. [1]

Figure $2.1.1$: Examples of Thermodynamic Systems.

In the first case, a liquid is contained in a typical Erlenmeyer flask. The boundaries of the system are the glass walls of the beaker. The second system is represented by the gas contained in a balloon. The boundary is a physical barrier also in this case, being the plastic of the balloon. The third case is that of a thunder cloud. The boundary is not a well-defined physical barrier, but rather some condition of pressure and chemical composition at the interface between the cloud and the atmosphere. Finally, the fourth case is the case of an open flame. In this case, the boundary is again non-physical, and possibly even harder to define than for a cloud. For example, we can choose to define the flame based on some temperature threshold, color criterion, or even some chemical one. Despite the lack of physical boundaries, the cloud and the flame—as portions of space containing matter—can be defined as a thermodynamic system.

A system can exchange exclusively mass, exclusively energy, or both mass and energy with its surroundings. Depending on the boundaries' ability to transfer these quantities, a system is defined as open, closed, or isolated. An open system exchanges both mass and energy. A closed system exchanges only energy, but not mass. Finally, an isolated system does not exchange mass nor energy.

When a system exchanges mass or energy with its surroundings, some of its parameters (variables) change. For example, if a system loses mass to the surroundings, the number of molecules (or moles) in the system will decrease. Similarly, if a system absorbs some energy, one or more of its variables (such as its temperature) increase. Mass and energy can flow into the system or out of the system. Let's consider mass exchange only. If some molecules of a substance leave the system, and then the same amount of molecules flow back into the system, the system will not be modified. We can count, for example, 100 molecules leaving a system and assign them the value of –100 in an outgoing process, and then observe the same 100 molecules going back into the system and assign them a value of +100. Regardless of the number of molecules present in the system in the first place, the overall balance will be –100 (from the outgoing process) +100 (from the ingoing process) = 0, which brings the system to its initial situation (mass has not changed). However, from a mathematical standpoint, we could have equally assigned the label +100 to the outgoing process and –100 to the ingoing one, and the overall total would have stayed the same: +100–100 = 0. Which of the two labels is best? For this case, it seems natural to define a mass going out of the system as negative (the system is losing it), and a mass going into the system as positive (the system is gaining it), but is it as straightforward for energy?

Table $2.1.1$

Type of System	**Mass**	**Energy** (either heat or work)
Open	Y	Y
Closed	N	Y

Type of System	Mass	Energy (either heat or work)
Isolated	N	N

Here is another example. Let's consider a system that is composed of your body. When you exercise, you lose mass in the form of water (sweat) and CO2 (from respiration). This mass loss can be easily measured by stepping on a scale before and after exercise. The number you observe on the scale will go down. Hence you have lost weight. After exercise, you will reintegrate the lost mass by drinking and eating. If you have reinstated the same amount you have lost, your weight will be the same as before the exercise (no weight loss). Nevertheless, which label do you attach to the amounts that you have lost and gained? Let's say that you are running a 5 km race without drinking nor eating, and you measure your weight dropping 2 kg after the race. After the race, you drink 1.5 kg of water and eat a 500 g energy bar. Overall you did not lose any weight, and it would seem reasonable to label the 2 kg that you've lost as negative (–2) and the 1.5 kg of water that you drank and the 500 g bar that you ate as positive (+1.5 +0.5 = +2). But is it the only way? After all, you didn't gain nor lose any weight, so why not calling the 2 kg due to exercise +2 and the 2 that you've ingested as –2? It might seem silly, but mathematically it would not make any difference, the total would still be zero. Now, let's consider energy instead of mass. To run the 5km race, you have spent 500 kcal, which then you reintegrate precisely by eating the energy bar. Which sign would you put in front of the kilocalories that you "burned" during the race? In principle, you've lost them, so if you want to be consistent, you should use a negative sign. But if you think about it, you've put quite an effort to "lose" those kilocalories, so it might not feel bad to assign them a positive sign instead. After all, it's perfectly OK to say, "I've done a 500 kcal run today", while it might sound quite awkward to say, "I've done a –500 kcal run today." Our previous exercise with mass demonstrates that it doesn't really matter which sign you put in front of the quantities. As long as you are consistent throughout the process, the signs will cancel out. If you've done a +500 kcal run, you've eaten a bar for –500 kcal, resulting in a total zero loss/gain. Alternatively, if you've done a –500 kcal run, you would have eaten a +500 kcal bar, for a total of again zero loss/gain.

These simple examples demonstrate that the sign that we assign to quantities that flow through a boundary is arbitrary (i.e., we can define it any way we want, as long as we are always consistent with ourselves). There is no best way to assign those signs. If you ask two different people, you might obtain two different answers. But we are scientists, and we must make sure to be rigorous. For this reason, chemists have established a convention for the signs that we will follow throughout this course. If we are consistent in following the convention, we are guaranteed to never make any mistake with the signs.

Definition: System-centric

The chemistry convention of the sign is system-centric:[2]

- If something (energy or mass) goes into the system it has a positive sign (the system is gaining)
- If something (energy or mass) goes out of the system it has a negative sign (the system is losing)

If you want a trick to remember the convention, use the weight loss/gain during the exercise example above. You are the system, if you lose weight, the kilograms will be negative (–2 kg), while if you gain weight, they will be positive (+2 kg). Similarly, if you eat an energy bar, you are the system, and you will have increased your energy by +500 kcal (positive). In contrast, if you burned energy during exercise, you are the system, and you will have lost energy, hence –500 kcal (negative). If the system is a balloon filled with gas, and the balloon is losing mass, you are the balloon, and you are losing weight; hence the mass will be negative. If the balloon is absorbing heat (likely increasing its temperature and increasing its volume), you are the system, and you are gaining heat; hence heat will be positive.

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1. The photos depicted in this figure are taken from Wikipedia: the Erlenmeyer flasks photo was taken by user Maytouch L., and distributed under CC-BY-SA license; the cloud photo was taken by user Mathew T Rader, and distributed under CC-BY-SA license; the flame picture was taken by user Oscar, and distributed under CC-BY-SA license; the balloon photo is in the public domain.
2. Notice that physicists use a different sign convention when it comes to thermodynamics. To eliminate confusion, I will not describe the physics convention here, but if you are reading thermodynamics on a physics textbook, or if you are browsing the web and stumble on thermodynamics formula (e.g., on Wikipedia), please be advised that some quantity, such as work, might have a different sign than the one that is used in this textbook. Obviously, the science will not change, but you need to be

always consistent, so if you decide that you want to use the physics convention, make sure to *always* use the physics convention. In this course, on the other hand, we will *always* use the chemistry one, as introduced above.

2.2: Internal Energy

The internal energy of a system is identified with the random, disordered motion of molecules; the total (internal) energy in a system includes potential and kinetic energy. This is contrast to external energy which is a function of the sample with respect to the outside environment (e.g. kinetic energy if the sample is moving or potential energy if the sample is at a height from the ground etc). The symbol for Internal Energy Change is ΔU.

Energy on a smaller scale

- Internal energy includes energy on a microscopic scale
- It is the sum of all the microscopic energies such as:
    1. translational kinetic energy
    2. vibrational and rotational kinetic energy
    3. potential energy from intermolecular forces

Example

One gram of water at zero °Celsius compared with one gram of copper at zero °Celsius do NOT have the same internal energy because even though their kinetic energies are equal, water has a much higher potential energy causing its internal energy to be much greater than the copper's internal energy.

Internal Energy Change Equations

The first law of thermodynamics states:

$$dU = dq + dw \tag{2.2.1}$$

where dq is heat and dw is work.

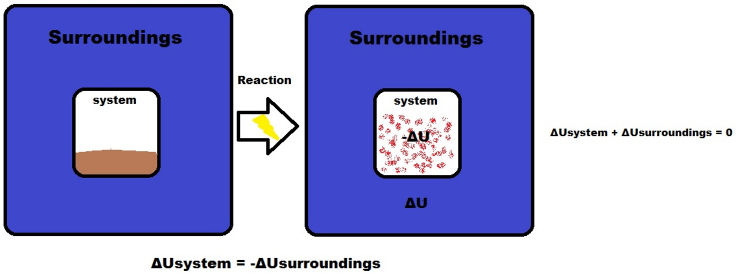
An isolated system cannot exchange heat or work with its surroundings making the change in internal energy equal to zero:

$$dU_{\text{isolated system}} = 0 \tag{2.2.2}$$

Therefore, in an isolated system:

$$dq = -dw \tag{2.2.3}$$

Energy is Conserved



$$dU_{\text{isolated system}} = dU_{\text{system}} + dU_{\text{surroundings}} \tag{2.2.4}$$

$$dU_{\text{system}} = -dU_{\text{surroundings}} \tag{2.2.5}$$

The signs of internal energy

- Energy *entering* the system is **POSITIVE (+)**, meaning heat is *absorbed*, **q>0**. Work is thus done *on* the system, **w>0**
- Energy *leaving* the system is **NEGATIVE (-)**, meaning heat is *given off* by the system, **q<0** and work is done *by* the system, **w<0**

Quick Notes

- A system *contains* ONLY Internal Energy
- A system does NOT *contain* energy in the form of heat or work
- Heat and work only exist during a change in the system; they are path functions
- Internal energy is a state function

Outside Links

- Levine, Ira N. "Thermodynamic internal energy of an ideal gas of rigid rotors." J. Chem. Educ. **1985**: 62, 53.

Contributors

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2.3: The Joule Experiment

Going back to the expression for changes in internal energy that stems from assuming that U is a function of V and T (or $U(V,T)$ for short)

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

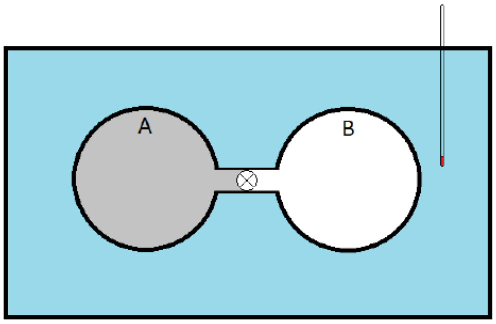
one quickly recognizes one of the terms as the constant volume heat capacity, C_V. And so the expression can be re-written

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT$$

But what about the first term? The partial derivative is a coefficient called the "internal pressure", and given the symbol π_T.

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

James Prescott Joule (1818-1889) recognized that π_T should have units of pressure (Energy/volume = pressure) and designed an experiment to measure it.



He immersed two copper spheres, A and B, connected by a stopcock. Sphere A is filled with a sample of gas while sphere B was evacuated. The idea was that when the stopcock was opened, the gas in sphere A would expand ($\Delta V > 0$) against the vacuum in sphere B (doing no work since $p_{ext} = 0$. The change in the internal energy could be expressed

$$dU = \pi_T dV + C_V dT$$

But also, from the first law of thermodynamics

$$dU = dq + dw$$

Equating the two

$$\pi_T dV + C_V dT = dq + dw$$

and since $dw = 0$

$$\pi_T dV + C_V dT = dq$$

Joule concluded that $dq = 0$ (and $dT = 0$ as well) since he did not observe a temperature change in the water bath which could only have been caused by the metal spheres either absorbing or emitting heat. And because $dV > 0$ for the gas that underwent the expansion into an open space, π_T must also be zero! In truth, the gas did undergo a temperature change, but it was too small to be detected within his experimental precision. Later, we (once we develop the *Maxwell Relations*) will show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{2.3.1}$$

Application to an Ideal Gas

For an ideal gas $p = RT/V$, so it is easy to show that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{2.3.2}$$

so combining Equations 2.3.1 and 2.3.2 together to get

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - p \tag{2.3.3}$$

And since also becuase $p = RT/V$, then Equation 2.3.3 simplifies to

$$\left(\frac{\partial U}{\partial V}\right)_T = p - p = 0$$

So while Joule's observation was consistent with limiting ideal behavior, his result was really an artifact of his experimental uncertainty masking what actually happened.

Appliation to a van der Waals Gas

For a van der Waals gas,

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \tag{2.3.4}$$

so

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} \tag{2.3.5}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V-b} - p \tag{2.3.6}$$

Substitution of the expression for p (Equation 2.3.4) into this Equation 2.3.6

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

In general, it can be shown that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

And so the internal pressure can be expressed entirely in terms of measurable properties

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

and need not apply to only gases (real or ideal)!

2.4: Enthalpy

Enthalpy

A Definition

In the previous section, we discussed several different process conditions, focusing first on isothermal expansions and contractions, and then on adiabatic, constant-volume calorimetry. In this section we will focus on constant pressure processes so that we can study the thermodynamic property enthalpy, H. Recall the definition of internal energy

$$U = q + w \tag{2.4.1}$$

Under constant volume conditions, the system could do no work, so

$$U = q_V \tag{2.4.2}$$

If the volume of the system is allowed to change, however, the system can do work as it expands against the external pressure, w will have a negative, non-zero value, and

$$U < q \tag{2.4.3}$$

Equation 2.4.1 can be rewritten as

$$U = q + (-PV) \tag{2.4.4}$$

where $w = -PV$ is always be negative if the system is constrained to do only expansion work.

Enthalpy (H) is defined as the sum of the internal energy (U) and the product of pressure and volume (PV):

$$H = U + PV \tag{2.4.5}$$

Enthalpy is a state function which depends entirely on the state functions V, P and U. It is not possible to measure absolute enthalpy, but the change in enthalpy (ΔH) for a process between initial and final states can be measured experimentally:

$$\Delta H = \Delta U + \Delta PV \tag{2.4.6}$$

If temperature and pressure remain constant through the process and the work is limited to pressure-volume work, then the enthalpy change is given by the equation:

$$\Delta H = \Delta U + P\Delta V \tag{2.4.7}$$

Note

Equation 2.4.7 can be derived starting with the basic premise of an infinitesimal change to the system:

$$H + dH = (U + dU) + (P + dP)(V + dV) \tag{2.4.8}$$

$$H + dH = U + dU + PV + VdP + PdV + dPdV \tag{2.4.9}$$

The VdP term is 0 because the process is carried out at constant pressure. The $dPdV$ term is so small (the product of two infinitesimal changes) that it can be approximated as 0. Thus Equation 2.4.9 becomes

$$H + dH = U + dU + PV + PdV \tag{2.4.10}$$

By the definition of Equation 2.4.5, $H = U + PV$, thus

$$H + dH = H + dU + PdV \tag{2.4.11}$$

which becomes

$$dH = dU + PdV \tag{2.4.12}$$

If the system undergoes a change from a fixed initial condition to a fixed final condition, then

$$\int dH = \int dU + P\int dV \tag{2.4.13}$$

resulting in

$$\Delta H = \Delta U + P\Delta V \tag{2.4.14}$$

Per the definition of the first law,

$$\Delta U = q + w \tag{2.4.15}$$

Because the constant-pressure work will always be expansion work against the surroundings, $w = -P\Delta V$, and

$$\Delta H = q_P + (-P\Delta V) + P\Delta V \tag{2.4.16}$$

We now can see that the change in enthalpy is the change in heat at constant pressure:

$$\Delta H = q_P \tag{2.4.17}$$

Example 2.4.1: Enthalpy Change Accompanying a Change in State

When a liquid vaporizes, the temperature remains constant because the liquid absorbs heat from its surroundings to replace the energy taken in by the vaporizing molecules as the intermolecular forces are broken. This heat required to vaporize the liquid is called enthalpy of vaporization (or heat of vaporization).

Suppose that a sample of methanol is heated to its boiling point at a constant pressure of 1.00 atm. An electric current of 0.750 amps from a 12.0 Volt power supply is passed through a coil for 250 seconds to add heat to the liquid. If 1.88 grams of methanol is converted to vapor by this process, what is the ΔH for this specific process, what is the ΔH_m for methanol?

Strategy: Use the Equation $q = I \cdot t \cdot \Delta\phi$ to calculate the energy used to vaporize the liquid, which is ΔH, and then divide by the number of moles to determine the molar enthalpy of vaporization.

Answer

$$q_P = \Delta H = (0.750 \frac{C}{s})(250 s)(12.0 \frac{J}{C}) = 2250 J$$

$$\Delta H_m = \left(\frac{2250\ J}{1.88\ grams}\right)\left(\frac{32.0\ grams}{1.00\ mole}\right)\left(\frac{1.00\ kJ}{1000\ J}\right) = 38.3 \frac{kJ}{mole}$$

Exercise 2.4.1

Suppose that a sample of water is heated to its boiling point at a constant pressure of 1.00 atm. An electric current of 0.850 amps from a 12.0 Volt power supply is passed through a coil for 150 seconds to add heat to the liquid. If 1.88 grams of water is converted to vapor by this process, what is the ΔH for this specific process, what is the ΔH_m for methanol?

Answer: ΔH = 1530 J, ΔH_m = 40.7 $\frac{kJ}{mole}$

Constant Pressure Calorimetry

It is relatively easy to measure an enthalpy change for a chemical or physical change that occurs at constant pressure. Often an insulated container such as a Styrofoam^{TM} cup can be used as the reaction vessel, with the atmosphere exerting the constant pressure. This type of calorimeter is called an **isobaric** calorimeter. A bomb calorimeter can be used to find ΔH for reactions involving solids and liquids because the molar volumes of solids and liquids are relatively small, leading to $\Delta H \approx \Delta U$. ΔH may differ greatly from ΔU for processes involving gases because of the large molar volumes of gases. For a reaction that involves a change in the number of moles of perfect gases Δn_g, under isothermal conditions,

$$\Delta H = \Delta U + \Delta n_g RT \tag{2.4.18}$$

Example 2.4.2: $\Delta H\ vs.\ \Delta U$

A) Solids

Calculate the difference between the ΔH_m and the ΔU_m for the conversion of graphite to diamond when the pressure is 1.0 bar. The density of graphite is 2.15 $\frac{grams}{cm^3}$ and the density of diamond is 3.51 $\frac{grams}{cm^3}$.

Strategy: You will need to use Equation 2.4.7 to solve this problem, with the understanding that ΔV_m can be found by dividing the molar mass M by the density ρ.

First, rearrange the Equation $\Delta H_m = \Delta U_m + P\Delta V_m$ to $\Delta H_m - \Delta U_m = P\Delta V_m$.

Next, realize that $\Delta V_m = V_{m,\ diamond} - V_{m,\ graphite}$

and therefore $\Delta V_m = \frac{M_{carbon}}{\rho_{diamond}} - \frac{M_{carbon}}{\rho_{graphite}}$

Answer: $\Delta H_m - \Delta U_m = P\left(\frac{M_{carbon}}{\rho_{diamond}} - \frac{M_{carbon}}{\rho_{graphite}}\right) = PM\left(\frac{1}{\rho_{diamond}} - \frac{1}{\rho_{graphite}}\right)$

$$\Delta H_m - \Delta U_m = (1.0x10^5 Pa)x(12.01\frac{grams}{mole})x\left(\frac{1.00cm^3}{3.51grams} - \frac{1.00cm^3}{2.15gram}\right)x\left(\frac{1.00\,m^3}{1.00x10^6\,cm^3}\right)x\left(\frac{1.00J)}{1.00Pa\cdot m^3}\right)$$

$$= -0.22\frac{J}{mole}$$

This is a small fraction of ΔH_m for the process, which is +1.9 kJ.

B) Gases

Calculate the difference between the ΔH_m and the ΔU_m for the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ at 298 K.

Strategy: Use Equation 2.4.18 to solve for $\Delta H_m - \Delta U_m = \Delta n_g RT$

Answer: $\Delta H_m - \Delta U_m = (-1mole)\,x\,0.008314\frac{kJ}{mole\cdot K}\,x\,(298K) = -2.48kJ$

Notice that the difference between ΔH and ΔU is much greater for a reaction involving the change in the number of moles of gases than it is for a phase change involving different solid forms of an element.

Exercise 2.4.2

A. Calculate the difference between the ΔH_m and the ΔU_m for the conversion of white phosphorus to black phosphorus when the pressure is 1.0 bar. The density of white phosphorus is 1.82 $\frac{grams}{cm^3}$ and the density of black phosphorus is 2.69 $\frac{grams}{cm^3}$.

Answer: $-0.55\frac{J}{mole}$

B. Calculate the difference between the ΔH_m and the ΔU_m for the reaction NH_3 (g) + HCl(g) $\rightleftharpoons$ NH_4Cl(s) at 298 K.

Answer: -4.96 kJ

The Relationship between Enthalpy and Temperature

It is often assumed that the enthalpy of a substance or a reaction is constant over a small range of temperatures. While this assumption is true, it is possible to calculate how much the enthalpy changes as the temperature changes. The manner in which the enthalpy varies as the temperature changes depends on whether the process is carried out under constant pressure or constant volume conditions.

ΔH vs. ΔT at Constant Pressure

The enthalpy of most systems increases as the temperature increases, and so a plot of enthalpy versus temperature results in a graph with a positive slope at any point. Each instantaneous slope is defined as the **heat capacity at constant pressure**, C_P. In other words,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.4.19}$$

As with the described in the derivation of the heat capacity at constant volume, C_V, Equation 2.4.19 is a partial derivative because the enthalpy of a system will typically vary with both pressure and temperature, but we are holding the pressure constant and allowing only the temperature to change.

Because C_P tells us the amount of heat needed to change the temperature of a sample of a substance at constant pressure, we can also say that an infinitesimal change in enthalpy is equal to an infinitesimal change in temperature multiplied by the heat capacity at constant pressure

$$dH = C_P\,dT \tag{2.4.20}$$

If the heat capacity of the substance does not change a great deal over the temperature range of interest, then the slope of the H versus T graph will be fairly constant. In this case

$$\Delta H = \int C_P\,dT = C_P\cdot(T_2 - T_1) = C_P\cdot\Delta T \tag{2.4.21}$$

As noted in Equation 2.4.17,

$$\Delta H = q_P \tag{2.2.17}$$

so that

$$q_P = C_P \cdot \Delta T \tag{2.4.22}$$

Equation 2.4.22 shows us that we can experimentally determine the constant pressure heat capacity of a substance fairly easily by measuring the change in temperature of a substance as heat is added to it under constant pressure conditions.

The value of C_P is an extensive property because it tells us how much heat is needed to change the temperature of that specific sample of the pure substance. We can determine the intensive property of this pure substance, the molar heat capacity at constant pressure, $C_{P,m}$, if we divide the experimentally obtained C_P by the number of moles of the substance used in the experiment:

$$C_{P,m} = \frac{C_P}{n} \tag{2.4.23}$$

We can also calculate a second intensive property, the specific heat capacity, $C_{P,s}$, which is the heat capacity per mass of sample:

$$C_{P,s} = \frac{C_P}{mass} \tag{2.4.24}$$

The value of C_P does actually change as the temperature changes. If it is necessary to estimate this change in value of C_P with a change in temperature, the following equation can be used:

$$C_{P,m} = a + bT + \frac{c}{T^2} \tag{2.4.25}$$

where the values of a, b, and c are temperature-independent and can be found in reference tables.

Example 2.4.3:

What is the change in molar enthalpy of CO_2 when it is heated from 20º C to 75º C? For CO_2 a = 44.22 J·mole^{-1}·K^{-1}, b = 8.79 x 10^{-3} J·mole^{-1}·K^{-2}, and c = -8.62 x 10^{5} J·mole^{-1}·K.

Strategy: Because C_P changes as the temperature changes, we must use Equation 2.4.21:

$$\Delta H = \int C_P \, dT = C_P \cdot (T_2 - T_1) = C_P \cdot \Delta T \tag{2.2.21}$$

determine the integral and evaluate the result over the range of temperatures.

Answer: $\Delta H_m = \int \left(a + bT + \frac{c}{T^2}\right) dT = H_m(T_2) - H_m(T_1) = a(T_2 - T_1) + \frac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$H_m\,(348K) - H_m\,(293K) = 44.22\frac{J}{mole \cdot K}(348K - 293K) + \frac{1}{2}\left(0.00879\frac{J}{mole \cdot K^2}\right)\left[(348K)^2 - (293K)^2\right]$

$- \left(-862,000\frac{J \cdot K}{mole}\right)\left(\frac{1}{348K} - \frac{1}{293K}\right) = 2120\frac{J}{mole} = 2.12\frac{kJ}{mole}$

Exercise 2.4.3

What is the change in molar enthalpy of CO_2 when it is heated from 10º C to 125º C? For CO_2 a = 44.22 J·mole^{-1}·K^{-1}, b = 8.79 x 10^{-3} J·mole^{-1}·K^{-2}, and c = -8.62 x 10^{5} J·mole^{-1}·K.

Answer: $4.55\frac{kJ}{mole}$

C_P vs. C_V

If the system of interest expands when heated under constant pressure conditions (as most systems do), then the system is doing work on the surroundings. In this case, less energy is acting to heat the system, and the temperature of the system increases less than it would if the system were held to a constant volume. A smaller increase in temperature indicates a higher heat capacity. Thus, in most cases, the constant pressure heat capacity is greater than the constant volume heat capacity,

$$C_P > C_V \tag{2.4.26}$$

For perfect gases

$$C_P - C_V = nR \tag{2.4.27}$$

Contributors and Attributions

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2.5: Thermochemistry

In this section, we will discuss the use of experimentally-determined enthalpy changes to predict the enthalpy changes in chemical reactions and physical changes that are of interest to us. As noted in previous sections, any process that releases energy is called an **exothermic** process. For example, when methane or propane is oxidized by O_2, the heat released causes the gas to expand, releasing heat and light, and doing work at the same time. If the process is carried out at constant pressure, this loss of energy represents a decrease in enthalpy ($\Delta H < 0$). An **endothermic** process absorbs energy, and in all cases, the energy is supplied from another source so that the enthalpy of the system increases ($\Delta H > 0$).

Standard Enthalpy Changes

In order to make the tabulated enthalpy data useful for scientific and engineering applications, there is a general agreement to report the enthalpy changes for a mole of a process at a set of standard conditions. For the vast majority of calculations, the accepted standard states, all at 1 bar pressure are:

- solids: pure solid
- liquids: pure liquid
- gases: pure gas
- solutes: 1 molal concentration $\dfrac{1\,mole\,solute}{kg\,solvent}$

There is no specific temperature associated with standard conditions. You must specify the temperature for the process of interest. For example, the standard state for water at 298 K is pure liquid water at 1 bar and 298 K. The standard state for water at 398 K is pure gas at 1 bar and 398 K. The conventional temperature for standard state enthalpy values that are found in reference tables is 298.15 K, but there are certainly tables of enthalpy values for different temperatures.

The **standard enthalpy change** for a process, ΔH^o, is defined as the change in enthalpy when the pure, separate reactants, in their standard states, change to the pure, separate products, in their standard states, at a specified temperature. This definition holds for physical changes and for chemical reactions.

> The **standard enthalpy change** for a process, ΔH^o, has the units of $\dfrac{kJ}{mole\,process}$, where a process is a physical change or a chemical reaction. This is often a confusing concept because the word "process" is often left out of the units. As will become clear later, the presence or absence of the word "process" depends on the context of the statement or question.

The following are examples of **thermochemical equations**, each of which is a combination of a process and its corresponding change in standard enthalpy:

$$H_2O(l) \rightarrow H_2O(g) \;\; \Delta H^o = 44.016\,kJ$$

$$H_2O(l) \rightarrow H_2O(g) \;\; \Delta H^o = 40.656\,kJ\,(373K)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \;\; \Delta H^o = -571.66\,kJ$$

The reactions might more clearly be written as

$$44.016\,kJ\, +\, H_2O(l) \rightarrow H_2O(g)$$

$$40.656\,kJ\, +\, H_2O(l) \rightarrow H_2O(g)\,@(373K)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)\, +\, 571.66\,kJ$$

Physical Changes

When a pure liquid vaporizes, or when a solid changes from one polymorph to another, a change in state occurs. These changes in state involve changes in enthalpy that are classified as **enthalpies of transition**. It is common practice to list **standard enthalpies of transition** as the enthalpy change per 1 mole of particles undergoing the transition at 1 bar pressure. For example, the standard enthalpy of fusion (ΔH^o_{fus}) for 1 mole of benzene at 278.6 K is written as

$$C_6H_6(s) \rightarrow C_6H_6(l)$$

with

$$\Delta H^o_{fus} = 10.59\,\frac{kJ}{mole}\,(278.6K)$$

Chemical Changes

A chemical change can be thought of as a process in which bonds between atoms in existing substances are broken and these atoms rearrange and/or reorganize to form the new bonds of different substances. To describe the enthalpy change of such a process it is common practice to list the **standard enthalpy of reaction**, ΔH^o_r which has the units of $\frac{kJ}{mole\,reaction}$.

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$

with

$$\Delta H^o_r = -92.22\,\frac{kJ}{mole}$$

is interpreted as 92.22 kJ of heat are given off per every 3 moles of H_2 consumed, every 1 mole of N_2 consumed, and every 2 moles of NH_3 produced.

A Few Rules

At 298 K, the combustion of 1.0 mole hydrogen with 0.5 moles of oxygen to form 1.0 mole of H_2O releases 285.8 kJ of energy. We represent the reaction:

$$\mathrm{H_{2(g)}} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O_{(l)}}, \quad \Delta H^o_r = -285.8\ \mathrm{kJ/mole}$$

For the reverse reaction, 285.8 kJ/mol is required, thus the sign for ΔH^o_r changes

$$\mathrm{H_2O_{(l)}} \rightarrow \mathrm{H_{2(g)}} + \frac{1}{2}\mathrm{O_2}, \quad \Delta H^o_r = +285.8\ \mathrm{kJ/mole}$$

It is also true that the amount of energy released in a chemical reaction is related to the amount of reactants. For example, when the amount of reactants is doubled, so is the amount of energy released.

$$\mathrm{2H_{2(g)}} + \mathrm{O_2} \rightarrow \mathrm{2H_2O_{(l)}}, \quad \Delta H^o_r = -571.66\ \mathrm{kJ/mole}$$

Example 2.5.1: Standard Enthalpy of Reaction

The standard enthalpy for the combustion of methane is -890. kJ per mole,

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g) \quad \Delta H^o_r = -890.\,kJ$$

Calculate the standard enthalpy change when 3.50 moles of oxygen are consumed during the conversion of methane to the gaseous products at 298 K.

Solution

When 2.00 moles of O_2, at 298 K and 1.00 bar, reacts with CH_4 according to the given equation, the standard enthalpy change is 890. kJ. Thus, the standard change of enthalpy when 3.50 moles of O_2 are used is

$$\Delta H^o_r = 3.50\,moles\,O_2 \times \frac{890.\,kJ}{2.00\,mole\,O_2} = -1560\,kJ\,.$$

Exercise 2.5.1

Calculate the standard change in enthalpy when 75.0 grams of Al are completely used up in the following reaction:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3 + 850kJ$$

Answer: ΔH^o_r = -1180 kJ

Standard Heats of Formation

Another way to look at ΔH^o_r is to state that

$$\Delta H_r^o = \sum_{products} vH_m^o - \sum_{reactants} vH_m^o \tag{2.5.1}$$

where v is the stoichiometric coefficient of each substance with the units of $\frac{moles\, substance}{moles\, reaction}$.

Equation 2.5.1 is of no use for practical applications because the values of absolute H_m^o are unknown. This inconvenience can be overcome by creating a self-consistent system in which definitions that are demonstrably incorrect can nevertheless be used to calculate ΔH_m^o values known as **standard enthalpies of formation**, ΔH_f^o. By definition, the ΔH_f^o of a substance is the enthalpy change the accompanies the formation of exactly 1 mole of the substance when the starting materials are the pure elements in their most stable form at the given set of conditions. The demonstrably incorrect aspect is that the ΔH_f^o of pure elements in their most stable allotrope under the given conditions is defined to be 0 $\frac{kJ}{mole}$, a tactic that will be explained later. A similar definition, instituted to allow for the determination of ΔH_f^o for ions in aqueous solutions, is that ΔH_f^o = 0 kJ for the hydrogen ion, H^+ (aq).

For example, at 298 K, the combustion of 1.0 mole hydrogen with 0.5 moles of oxygen to form 1.0 mole of H_2O releases 286 kJ of energy. We represent the reaction:

$$\mathrm{H_{2(g)}} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O_{(l)}}, \quad \Delta H_f^o = -286\ \mathrm{kJ/mol}$$

The following table shows several reactions that fit into the category of standard enthalpy of formation reactions:

$$\mathrm{Mg_{(s)}} + \frac{1}{8}\mathrm{S_{8(s)}} \rightarrow \mathrm{MgS_{(s)}} \qquad \Delta H_f^\circ = -598\ \mathrm{kJ/mol} \tag{2.5.2}$$

$$\mathrm{P_{(s)}} + \frac{3}{2}\mathrm{Cl_{2(g)}} \rightarrow \mathrm{PCl_{3(g)}} \qquad \Delta H_f^\circ = -320\ \mathrm{kJ/mol} \tag{2.5.3}$$

$$\mathrm{P_{(s)}} + \frac{5}{2}\mathrm{Cl_{2(g)}} \rightarrow \mathrm{PCl_{5(g)}} \qquad \Delta H_f^\circ = -440\ \mathrm{kJ/mol} \tag{2.5.4}$$

$$\mathrm{H_{2(g)}} + \frac{1}{2}\mathrm{O_{2(g)}} \rightarrow \mathrm{H_2O_{(l)}} \qquad \Delta H_f^\circ = -286\ \mathrm{kJ/mol} \tag{2.5.5}$$

$$\frac{1}{2}\mathrm{N_{2(g)}} + \mathrm{O_{2(g)}} \rightarrow \mathrm{NO_{2(g)}} \qquad \Delta H_f^\circ = +34\ \mathrm{kJ/mol} \tag{2.5.6}$$

$$\mathrm{Cu_{(s)}} + \frac{1}{2}\mathrm{O_{2(g)}} \rightarrow \mathrm{CuO_{(s)}} \qquad \Delta H_f^\circ = -157\ \mathrm{kJ/mol} \tag{2.5.7}$$

$$\mathrm{Mg_{(s)}} + \frac{1}{2}\mathrm{O_{2(g)}} \rightarrow \mathrm{MgO_{(s)}} \qquad \Delta H_f^\circ = -602\ \mathrm{kJ/mol} \tag{2.5.8}$$

$$\mathrm{C_{(graphite)}} + \mathrm{O_{2(g)}} \rightarrow \mathrm{CO_{2(g)}} \qquad \Delta H_f^\circ = -394\ \mathrm{kJ/mol} \tag{2.5.9}$$

$$\mathrm{C_{(graphite)}} + 4\mathrm{H_{2(g)}} \rightarrow \mathrm{CH_{4(g)}} \qquad \Delta H_f^\circ = -75\ \mathrm{kJ/mol} \tag{2.5.10}$$

In all the above equations of reaction, the right hand side has only one product and its coefficient is 1. To obtain a balanced equation, it is often necessary to use fractional coefficients for the pure element reactants, which is allowed because all of the reactions are taking place on the molar scale. (Thermodynamics is a study of **macroscopic** systems.) Because all standard enthalpy of formation reactions are, by definition, the formation of 1 mole of a pure substance from its component elements in their most stable form under the reaction conditions, we often do not write out the entire equation, but instead simply write

$$\Delta H_f^o\, MgS(s) = -598\, \frac{kJ}{mole\, MgS}$$

Note

The use of ΔH_f^o values to calculate ΔH_r^o values is made possible by assuming that any chemical reaction can be broken down into two distinct , hypothetical steps:

Step 1) All of the reactants decompose ("unform") to produce the pure elements of which they are composed.

Step 2) All of the pure elements created in Step 1 react to form the products of the overall reaction.

If these hypothetical steps are assumed to occur, it is perfectly legitimate (although absolutely incorrect) to assign all of the pure elements a ΔH_f^o = 0 kJ. For example, even though we know that 436 kJ is released when 2 moles of H atoms react to form 1 mole of H_2 , we can proceed with the erroneous assumption that the ΔH_f^o of H_2 = 0 kJ because the ΔH_f^o of every hydrogen-containing compound will incorporate this erroneous value of ΔH_f^0 of H_2. Thus, the ΔH_f^o of H_2O incorporates not only the enthalpy change associated with the formation of the bonds in H_2O, but also the enthalpy change associated with the breaking of bonds in H_2 and in O_2.

When calculating both the change in enthalpy for Step 1 and the change in enthalpy for Step 2 of any reaction, the incorrect assignment of a value of 0 kJ will be canceled out as we first "unform" reactants and then form products. (Two wrongs make a right in this case!) The following calculation will show this point:

Calculate the ΔH_r^o for the reaction $CH_4\,(g) + 2\,O_2\,(g) \rightarrow 2\,H_2O\,(g) + CO_2\,(g)$, given the data: ΔH_f^o H_2O = -286 $\dfrac{kJ}{mole}$; ΔH_f^o CO_2 = -394 $\dfrac{kJ}{mole}$; ΔH_f^o CH_4 = -75 $\dfrac{kJ}{mole}$.
Step 1: Unforming reactants $CH_4\,(g) + 2\,O_2\,(g) \rightarrow C\,(graphite) + 2H_2\,(g) + 2\,O_2\,(g)$

Step 2: Forming products $C\,(graphite) + 2H_2\,(g) + 2\,O_2\,(g) \rightarrow 2\,H_2O\,(g) + CO_2\,(g)$

It is not possible to obtain a thermodynamically precise value of \(\Delta H^o_f)\ for a substance by adding up the contribution of each of the bonds in the substance. For instance, the \(\Delta H^o_f)\ for CH_4 can not be precisely approximated by adding up the energy released by the formation of 4 C - H bonds. The attempts fails because the ΔH of a C - H bond differs from compound to compound, and even within a compound. (For instance, the energy needed to break the first C - H bond in CH_4 is different from the energy needed to break the second C - H bond in the remaining CH_3 particle.) Molecular modeling with computers has improved the approximated bond energies, but experimentation is still the most reliable technique to determine precise values for \(\Delta H^o_f)\.

Given the concept of ΔH_f^o, it is possible to re-write equation 2.5.1 as

$$\Delta H_r^o = \sum_{products} v\Delta H_f^o - \sum_{reactants} v\Delta H_f^o \tag{2.5.11}$$

in which we use the standard enthalpies of formation to calculate the standard enthalpy of reaction.

To demonstrate the use of tabulated ΔH^o_f values, we will use them to calculate ΔH_{rxn} for the combustion of glucose:

$$C_6H_{12}O_6\,(s) + O_2\,(g) \rightarrow CO_2\,(g) + 6H_2O\,(l) \tag{2.5.12}$$

Using Equation 2.5.11, we write

$$\Delta H_r^o = \left\{6\Delta H_f^o\,[CO_2\,(g)] + 6\Delta H_f^o\,[H_2O\,(g)]\right\} - \left\{6\Delta H_f^o\,[C_6H_{12}O_6\,(s)] + 6\Delta H_f^o\,[O_2\,(g)]\right\} \tag{2.5.13}$$

The relevant ΔH^o_f values are ΔH^o_f [CO_2(g)] = -393.5 kJ/mol, ΔH^o_f [H_2O(l)] = -285.8 kJ/mol, and ΔH^o_f [$C_6H_{12}O_6$(s)] = -1273.3 kJ/mol. Because O_2(g) is a pure element in its standard state, ΔH^o_f [O_2(g)] = 0 kJ/mol. Inserting these values into Equation 2.5.13 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\begin{aligned}\Delta H^o_{comb} &= [6\,(-393.5\;kJ/mol) + 6\,(-285.8\;kJ/mol)] \\ &- [-1273.3 + 6\,(0\;kJ\;mol)] = -2802.5\;kJ/mol\end{aligned} \tag{2.5.14}$$

As illustrated in Figure 2.5.1, we can use Equation 2.5.11 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb} The alternative hypothetical pathway consists of four separate reactions that convert the reactants *to the elements* in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}\Delta H_1^o = \Delta H_f^o\,[glucose\,(s)] = -1\;\; mol\;\cancel{glucose}\left(\frac{1273.3\;kJ}{1\;\;mol\;\cancel{glucose}}\right) = +1273.3\;kJ \\ \Delta H_2^o = 6\Delta H_f^o\,[O_2\,(g)] = 6\;\; mol\;\cancel{O_2}\left(\frac{0\;kJ}{1\;\;mol\;\cancel{O_2}}\right) = 0\;kJ\end{aligned} \tag{2.5.15}$$

(Recall that when we reverse a reaction, we must also reverse the sign of the accompanying enthalpy change.) The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

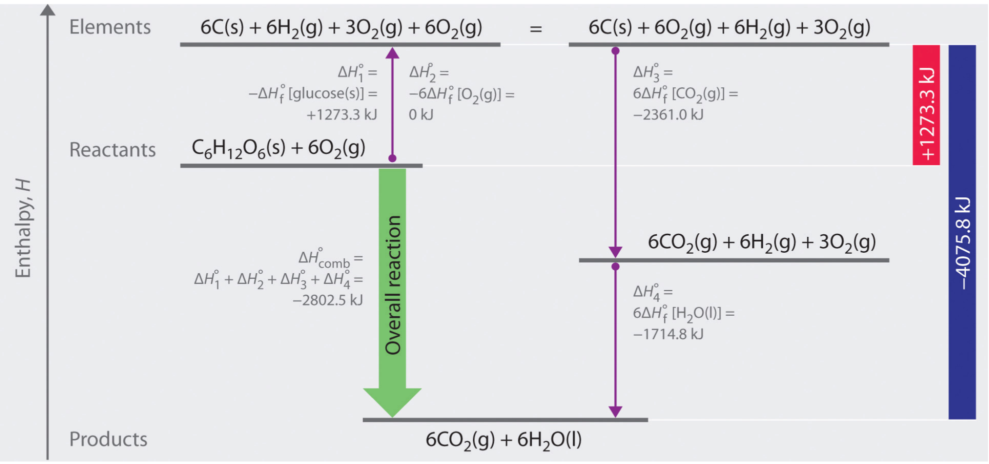

Figure 2.5.1*: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled $\Delta H^o{}_{comb}$ indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled $\Delta H^o{}_1$ and $\Delta H^o{}_2$). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled $\Delta H^o{}_3$ and $\Delta H^o{}_4$). Because enthalpy is a state function, $\Delta H^o{}_{comb}$ is equal to the sum of the enthalpy changes $\Delta H^o{}_1 + \Delta H^o{}_2 + \Delta H^o{}_3 + \Delta H^o{}_4$.*

The reactions that convert the elements to final products (downward purple arrows in Figure 2.3.1) are identical to those used to define the $\Delta H^o{}_f$ values of the products. Consequently, the enthalpy changes are

$$\begin{aligned} \Delta H_3^o &= \Delta H_f^o\left[CO_2\left(g\right)\right] = 6 \;\; mol \; \cancel{CO_2} \left(\frac{393.5 \; kJ}{1 \;\; mol \; \cancel{CO_2}}\right) = -2361.0 \; kJ \\ \Delta H_4^o &= 6\Delta H_f^o\left[H_2O\left(l\right)\right] = 6 \;\; mol \; \cancel{H_2O} \left(\frac{-285.8 \; kJ}{1 \;\; mol \; \cancel{H_2O}}\right) = -1714.8 \; kJ \end{aligned} \tag{2.5.16}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H_{comb}^o = +1273.3 \; kJ + (-4075.8 \; kJ) = -2802.5 \; kJ \tag{2.5.17}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 2.5.11) and $\Delta H^o{}_f$ values. The two results must be the same because Equation 2.5.17 is just a more compact way of describing the thermochemical cycle shown in Figure 2.5.1.

Example 2.5.2

Long-chain fatty acids such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] are one of the two major sources of energy in our diet (ΔH^of =−891.5 kJ/mol). Use the appropriate data to calculate $\Delta H^o{}_r$ for the combustion of 1 mole of palmitic acid.

Given: compound and $\Delta H^o{}_f$ values

Asked for: $\Delta H^o{}_r$ per mole

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 2.5.11 and the $\Delta H^o{}_f$ values for H_2O(l) and CO_2 (g) to calculate $\Delta H^o{}_r$, the energy released by the combustion of 1 mol of palmitic acid.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH°$_r$. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)} \tag{2.5.18}$$

Using Equation 2.5.11 with ΔH°$_f$ values (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned} \Delta H_r^o &= \sum m \Delta H^o{}_f\,(products) - \sum n \Delta H^o{}_f\,(reactants) \\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\ )] \\ &\quad - [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\ )] \\ &= -9977.3\ kJ/mol \end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

Exercise 2.5.2

Calculate ΔH°$_r$ for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

$$\begin{pmatrix} CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g) \\ water-gas\ shift\ reaction \end{pmatrix}$$

Answer:

−41.2 kJ/mol

Hess's Law

Hess's Law of Constant Heat Summation (or just **Hess's Law**) states that regardless of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes. This law is a manifestation of enthalpy as a state function, which allows us to calculate the overall change in enthalpy by simply summing up the changes for each step of the way, until the desired product is formed. All steps have to proceed under the same reaction conditions and the equations for the individual steps must balance out. The principle underlying Hess's law does not just apply to enthalpy and can be used to calculate other state functions like changes in Gibbs' free energy and entropy.

Definition: Hess's Law

The heat of any reaction ΔH_r° for a specific reaction is equal to the sum of the heats of reaction for any set of reactions which in sum are equivalent to the overall reaction:

Application

Hydrogen gas, which is of potential interest nationally as a clean fuel, can be generated by the reaction of carbon (coal) and water:

$$C_{(s)} + 2H_2O_{(g)} \rightarrow CO_{2\,(g)} + 2H_{2\,(g)} \tag{2.5.19}$$

Calorimetry reveals that this reaction requires the input of 90.1 kJ of heat for every mole of $C_{(s)}$ consumed. By convention, when heat is absorbed during a reaction, we consider the quantity of heat to be a positive number: in chemical terms, $q > 0$ for an endothermic reaction. When heat is evolved, the reaction is exothermic and $q < 0$ by convention.

It is interesting to ask where this input energy goes when the reaction occurs. One way to answer this question is to consider the fact that the reaction converts one fuel, $C_{(s)}$, into another, $H_{2(g)}$. To compare the energy available in each fuel, we can measure the heat evolved in the combustion of each fuel with one mole of oxygen gas. We observe that

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{2.5.20}$$

produces $393.5\ kJ$ for one mole of carbon burned; hence $q = -393.5\ kJ$. The reaction

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{2.5.21}$$

produces 483.6 kJ for two moles of hydrogen gas burned, so q=-483.6 kJ. It is evident that more energy is available from combustion of the hydrogen fuel than from combustion of the carbon fuel, so it is not surprising that conversion of the carbon fuel to hydrogen fuel requires the input of energy. Of considerable importance is the observation that the heat input in equation 2.5.19, 90.1 kJ, is exactly equal to the difference between the heat evolved, -393.5 kJ, in the combustion of carbon and the heat evolved, -483.6 kJ, in the combustion of hydrogen. This is not a coincidence: if we take the combustion of carbon and add to it the reverse of the combustion of hydrogen, we get

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

$$C_{(s)} + O_{2(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 2H_{2(g)} + O_{2(g)} \tag{2.5.22}$$

Canceling the $O_{2(g)}$ from both sides, since it is net neither a reactant nor product, equation 2.5.22 is equivalent to equation 2.5.19. Thus, taking the combustion of carbon and "subtracting" the combustion of hydrogen (or more accurately, adding the reverse of the combustion of hydrogen) yields equation 2.5.19. And, the heat of the combustion of carbon minus the heat of the combustion of hydrogen equals the heat of equation 2.5.19. By studying many chemical reactions in this way, we discover that this result, known as Hess's Law, is general.

Why it works

A pictorial view of Hess's Law as applied to the heat of equation 2.5.19 is illustrative. In figure 2.3.1, the reactants C(s) + 2 H_2O(g) are placed together in a box, representing the state of the materials involved in the reaction prior to the reaction. The products CO_2(g) + 2 H_2(g) are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing C(s), O_2(g), and 2 H_2(g). This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in equation 2.5.20 and equation 2.5.21.

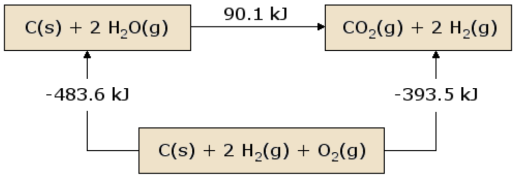

***Figure 1**: A Pictorial View of Hess's Law.*

This picture of Hess's Law reveals that the heat of reaction along the "path" directly connecting the reactant state to the product state is exactly equal to the total heat of reaction along the alternative "path" connecting reactants to products via the intermediate state containing $C_{(s)}$, $O_{2(g)}$, and 2 $H_{2(g)}$. A consequence of our observation of Hess's Law is therefore that the net heat evolved or absorbed during a reaction is independent of the path connecting the reactant to product (this statement is again subject to our restriction that all reactions in the alternative path must occur under constant pressure conditions).

Extensive tables of ΔH°r values have been compiled that allow us to calculate the heat of reaction for any reaction of interest, even including hypothetical reactions which may be difficult to perform or impossibly slow to react. The following reactions are examples of such $\Delta H°_r$ reactions:

$$2H_{(g)} \rightarrow H_{2(g)} \qquad \Delta H^\circ = -436\ \mathrm{kJ/mol} \tag{2.5.23}$$

$$2O_{(g)} \rightarrow O_{2(g)} \qquad \Delta H^\circ = -498\ \mathrm{kJ/mol} \tag{2.5.24}$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H^\circ = 44\ \mathrm{kJ/mol\ at\ 298\ K} \tag{2.5.25}$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H = 41\ \mathrm{kJ/mol\ at\ 373\ K},\ \text{non-standard condition} \tag{2.5.26}$$

$$Mg_{(s)} + S_{(s)} \rightarrow MgS_{(s)} \qquad \Delta H^\circ = -598\ \mathrm{kJ/mol} \tag{2.5.27}$$

$$2H_{(g)} + O_{(g)} \rightarrow H_2O_{(g)} \qquad \Delta H^\circ = -847\ \mathrm{kJ/mol} \tag{2.5.28}$$

$$Cu_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CuO_{(s)} \qquad \Delta H^\circ = -157\ \mathrm{kJ/mol} \tag{2.5.29}$$

$$\frac{1}{2}N_{2(g)} + O_{2(g)} \rightarrow NO_{2(g)} \qquad \Delta H^\circ = 34\ \mathrm{kJ/mol} \tag{2.5.30}$$

$$Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} \qquad \Delta H^\circ = -602\ \mathrm{kJ/mol} \tag{2.5.31}$$

$$2P_{(s)} + 3Cl_{2(g)} \rightarrow 2PCl_{3(s)} \qquad \Delta H^\circ = -640\ \mathrm{kJ/mol} \tag{2.5.32}$$

$$2P_{(s)} + 5Cl_{2(g)} \rightarrow 2PCl_{5(s)} \qquad \Delta H^\circ = -880\ \mathrm{kJ/mol} \tag{2.5.33}$$

$$C_{(graphite)} + 2O_{(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -643\ \mathrm{kJ/mol} \tag{2.5.34}$$

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -394\ \mathrm{kJ/mol} \tag{2.5.35}$$

$$C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \Delta H^\circ = -75\ \mathrm{kJ/mol} \tag{2.5.36}$$

$$2Al_{(s)} + Fe_2O_{3(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(s)} \qquad \Delta H^\circ = -850\ \mathrm{kJ/mol} \tag{2.5.37}$$

Example 2.5.3: Solving for Standard Enthalpy of Reaction Using Hess's Law

QUESTION

Calculate the standard enthalpy of combustion of the transition of C(s, graphite) → C(s, diamond), **given**

$$\mathrm{C(s, graphite)} + O_2 \longrightarrow CO_2 \quad \Delta H_r^o = -393.5 kJ/mol \tag{2.5.38}$$

$$CO_2 \longrightarrow C_{(s,diamond)} + O_2 \quad \Delta H_r^o = +395.41 kJ/mol \tag{2.5.39}$$

Solution

1. Find appropriate reactions and their standard enthalpy reaction
2. Flip reactions and/or multiply reactions, if necessary, so that the combination of reactions results in the desired overall reaction
3. Change the sign and/or magnitude of the ΔH_r^o values of the combined reactions, based on how the combined reactions were manipulated in Step 2
4. Sum up the individual steps and sum up the individual ΔH_r^o values to obtain the ΔH_r^o value of the desired reaction.

Answer

In this case, there is no need to flip an equation around because it is possible to cancel out terms as the reactions are given. What is left is canceling out the O_2 and the CO_2 species, writing the overall reaction and then summing the two reaction enthalpies together.

C(s, graphite) + ~~O_2~~ → ~~CO_2~~

~~CO_2~~ → C(s, diamond) + ~~O_2~~

$$C_{(s,graphite)} \rightarrow C_{(s,diamond)}$$

Adding the enthalpies gives (-393.5 kJ/mol + 395.41 kJ/mol) = +1.91 kJ/mol. Since the \(\Delta H^o_r\) is positive, the reaction is **endothermic**.

Exercise 2.5.3: Steam Reforming

Steam reforming is a method for producing hydrogen, carbon monoxide, or other useful products from hydrocarbon fuels such as natural gas. Use Hess's Law to calculate the following enthalpy of reaction of the major process of steam reforming:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \tag{2.5.40}$$

Given the separate reactions of carbon dioxide and hydrogen gas and methane decomposition;

$$CO_{(g)} + H_{2(g)} \rightarrow C_{(graphite)} + H_2O_{(g)} \quad \Delta H^\circ = -131.3\ kJ \tag{2.5.41}$$

$$C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \Delta H^\circ = -74.8\ kJ \tag{2.5.42}$$

$$CH_{4(g)} + H_2O \rightarrow CO + 3H_2 \quad \Delta H^\circ = +74.8\ kJ + 131.3\ kJ \tag{2.5.43}$$

Answer

$CH_{4(g)} + H_2O \rightarrow CO + 3H_2 \quad \Delta H_r^\circ = 201.1\ kJ$

Hence, it is not surprising that this reforming reactions takes place at high temperatures.

The Temperature Dependence of ΔH_r^o

For educational purposes most textbooks list thermodynamic values such as ΔH_f^o and ΔH_r^o for processes occurring at 298 K. It is obvious that not all reactions occur at this temperature. More advanced texts and reference books may have tables of thermodynamic data at temperatures other than 298 K, but they do not have values for all temperatures. Kirchhoff's Law can be used to accurately estimate the standard enthalpy of reaction at an elevated temperature if the standard enthalpy of reaction and the constant pressure heat capacity are known.

Kirchhoff's law is

$$\Delta H_r^o(T_2) = \Delta H_r^o(T_1) + \int \Delta_r C_P^o \, dT \tag{2.5.44}$$

where $T_2 > T_1$, the C_P values of the products and reactants do not change much over the temperature range from T_1 to T_2, and $\Delta_r C_P^o$ is the difference between the constant pressure molar heat capacities of the products and reactants, weighted by their stoichiometric coefficients:

$$\Delta_r C_{P,m}^o = \sum_{products} v C_{P,m}^o - \sum_{reactants} v C_{P,m}^o \tag{2.5.45}$$

where v is the stoichiometric coefficient of each substance.

If $\Delta_r C_{P,m}^o$ remains constant over the temperature range, then equation 2.5.44 becomes

$$\Delta H_r^o(T_2) = \Delta H_r^o(T_1) + (T_2 - T_1)\Delta_r C_{P,m}^o \tag{2.5.46}$$

Example 2.5.4:

The ΔH_f^o for H_2O (l) at 298 K is -286 $\frac{kJ}{mole}$. Estimate the value of ΔH_f^o for H_2O (l) at 350 K. The constant pressure molar heat capacities of the reactants and products are: H_2O (l) = 75.29 $\frac{J}{K \cdot mole}$; H_2 (g) = 28.84 $\frac{J}{K \cdot mole}$; O_2 (g) = 29.37 $\frac{J}{K \cdot mole}$. It is assumed that these values do not change over the given temperature range.

Given: ΔH_f^o H_2O (l) at 298 and $C_{P,m}^o$ values for the reactants and products.

Asked for: ΔH_f^o H_2O (l) at 350 K

Strategy: Use equation 2.5.45 to determine the $\Delta_r C_{P,m}^o$ for the reaction, then substitute this value into equation 2.5.46.

Solution: The reaction is $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

Thus, $\Delta_r C^o_{P,m} = C^o_{P,m}(H_2O,l) - \left(C^o_{P,m}(H_2,g) + \frac{1}{2}C^o_{P,m}(O_2,g)\right)$

and $\Delta_r C^o_{P,m} = 75.29\frac{J}{K \cdot mole} - \left(28.84\frac{J}{K \cdot mole} + \frac{1}{2}29.37\frac{J}{K \cdot mole}\right) = 31.77\frac{J}{K \cdot mole} = 0.03177\frac{kJ}{K \cdot mole}$

Then, $\Delta H^o_f(H_2O(l), 350K) = -286\frac{kJ}{mole} + (350K - 298K)\left(0.03177\frac{J}{K \cdot mole}\right) = -284\frac{kJ}{mole}$

This is not a large change, but it may be significant depending what you are trying to measure.

Exercise 2.5.4

The ΔH^o_f for H_2O (g) at 298 K is -241.8 $\frac{kJ}{mole}$. Estimate the value of ΔH^o_f for H_2O (l) at 400 K. The constant pressure molar heat capacities of the reactants and products are: H_2O (g) = 33.58 $\frac{J}{K \cdot mole}$; H_2 (g) = 28.84 $\frac{J}{K \cdot mole}$; O_2 (g) = 29.37 $\frac{J}{K \cdot mole}$. It is assumed that these values do not change over the given temperature range.

Answer: -242.8 kJ/mole

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2.6: Reaction Enthalpies

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

Example 2.6.1:

Find ΔH_{rxn} for the reaction

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

Given

$$C(gr) + ½O_2(g) \rightarrow CO(g)$$

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

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

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

Solution

The target reaction can be generated from the data reactions.

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

plus

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

equals

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

so

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

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

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

Standard Enthalpy of Formation

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

Definition: the Standard State

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

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

- $NaCl(s)$:

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

  with $\Delta H_f^o = -411.2\, kJ/mol$
- $C_3H_8(g)$:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned} \Delta_{rxn} &= (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) && (2.6.1) \\ &= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) - (1\, mol)\,(-74.6\, kJ/mol) && (2.6.2) \\ &= -890.5\, kJ/mol && (2.6.3) \end{aligned}$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization, fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane

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

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

Ionization Reactions

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Average Bond Enthalpies

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

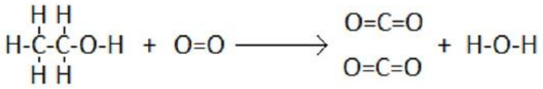
$$XY(g) \rightarrow X(g) + Y(g)$$

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

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

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

As an example, consider the combustion of ethanol:



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

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

The reaction enthalpy is then given by

$$\begin{aligned} \Delta H_c &= 5(413\, kJ/mol) + 1(348\, kJ/mol) + 1(358\, kJ/mol) \\ &\quad + 1(495\, kJ/mol) - 4(799\, kJ/mol) - 2(463\, kJ/mol) \\ &= -856\, kJ/mol \end{aligned} \tag{2.6.4}$$

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

2.7: Lattice Energy and the Born-Haber Cycle

An important enthalpy change is the Lattice Energy, which is the energy required to take one mole of a crystalline solid to ions in the gas phase. For $\mathrm{NaCl(s)}$, the lattice energy is defined as the enthalpy of the reaction

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(g)} + \mathrm{Cl^-(g)}$$

with ΔH called the lattice energy (ΔH_{Lat}).

The Born-Haber Cycle

A very handy construct in thermodynamics is that of the thermodynamic cycle. This can be represented graphically to help to visualize how all of the pieces of the cycle add together. A very good example of this is the **Born-Haber cycle**, describing the formation of an ionic solid.

Two pathways can be envisioned for the formation. Added together, the two pathways form a cycle. In one pathway, the ionic solid if formed directly from elements in their standard states.

$$\mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2} \rightarrow \mathrm{NaCl(s)}$$

with $\Delta H_f(NaCl)$.

The other pathway involves a series of steps that take the elements from neutral species in their standard states to ions in the gas phase.

$$Na(s) \rightarrow Na(g)$$

with $\Delta H_{sub}(Na)$

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

with $1^{st}\ IP(Na)$

$$½Cl_2(g) \rightarrow Cl(g)$$

with $½D(Cl-Cl)$

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

with $1^{st}\ EA(Cl)$

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$$

with $\Delta H_{Lat}(NaCl)$

It should be clear that when added (after proper manipulation if needed), the second set of reactions yield the first reaction. Because of this, the total enthalpy changes must all add.

$$\Delta H_{sub}(Na) + 1^{st}\ IP(Na) + ½D(Cl-Cl) + 1^{st}\ EA(Cl) + \Delta H_{lat}(NaCl) = \Delta H_f(NaCl)$$

This can be depicted graphically, the advantage being that arrows can be used to indicate endothermic or exothermic changes. An example of the Born-Haber Cycle for NaCl is shown below.

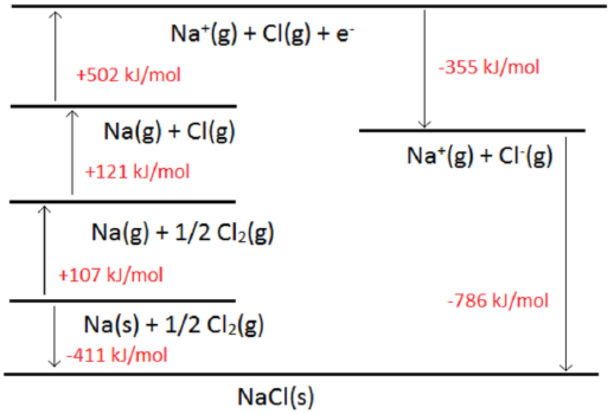


Figure 3.6.1: the Born-Haber Cycle for NaCl.

In many applications, all but one leg of the cycle is known, and the job is to determine the magnitude of the missing leg.

✓ Exercise 2.7.1: Potassium Bromide

Find ΔH_f for KBr given the following data.

$$\mathrm{K(s) \rightarrow K(g)}$$

with $\Delta H_{sub} = 89\, kJ/mol$

$$\mathrm{Br_2(l) \rightarrow Br_2(g)}$$

with $\Delta H_{vap} = 31\, kJ/mol$

$$\mathrm{Br_2(g) \rightarrow 2\, Br(g)}$$

with $D(Br-Br) = 193\, kJ/mol$

$$\mathrm{K(g) \rightarrow K^+(g) + e^-}$$

with $1^{st}\, IP(K) = 419 kJ/mol$

$$\mathrm{Br(g) + e^- \rightarrow Br-(g)}$$

with $1^{st}\, EA(Br) = 194 kJ/mol$

$$\mathrm{K^+(g) + Br-(g) \rightarrow KBr(s)}$$

with $\Delta H_{Lat} = 672 kJ/mol$

Answer

$\Delta H_f = -246\, kJ/mol$

Note: This cycle required the extra leg of the vaporization of Br_2. Many cycles involve ions with greater than unit charge and may require extra ionization steps as well!

2.8: Energy Basics

Learning Objectives

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure $2.8.1$). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.


(a) (b) (c)

Figure $2.8.1$: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by “Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 2.8.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.

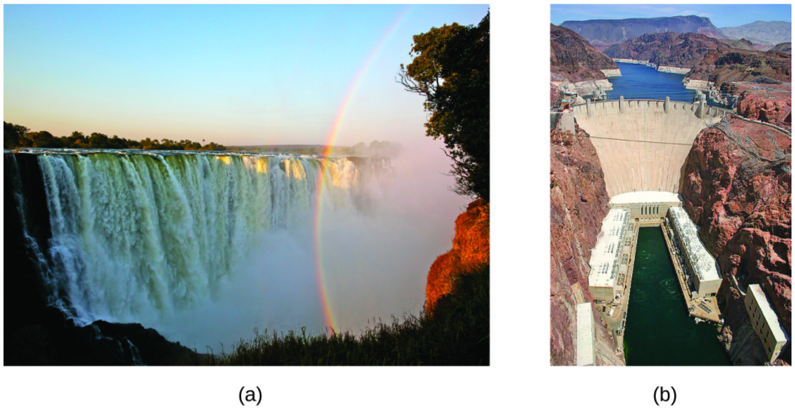


Figure 2.8.2: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons).

Two pictures are shown and labeled a and b. Picture a shows a large waterfall with water falling from a high elevation at the top of the falls to a lower elevation. The second picture is a view looking down into the Hoover Dam. Water is shown behind the high wall of the dam on one side and at the base of the dam on the other.

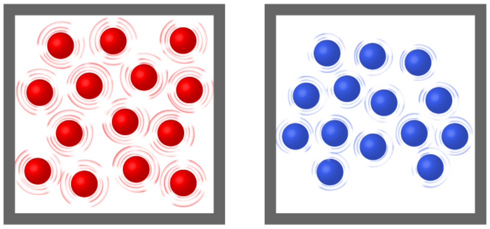
Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car’s engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders’ pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is “hot.” When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is “cold” (Figure 2.8.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.



Hot water

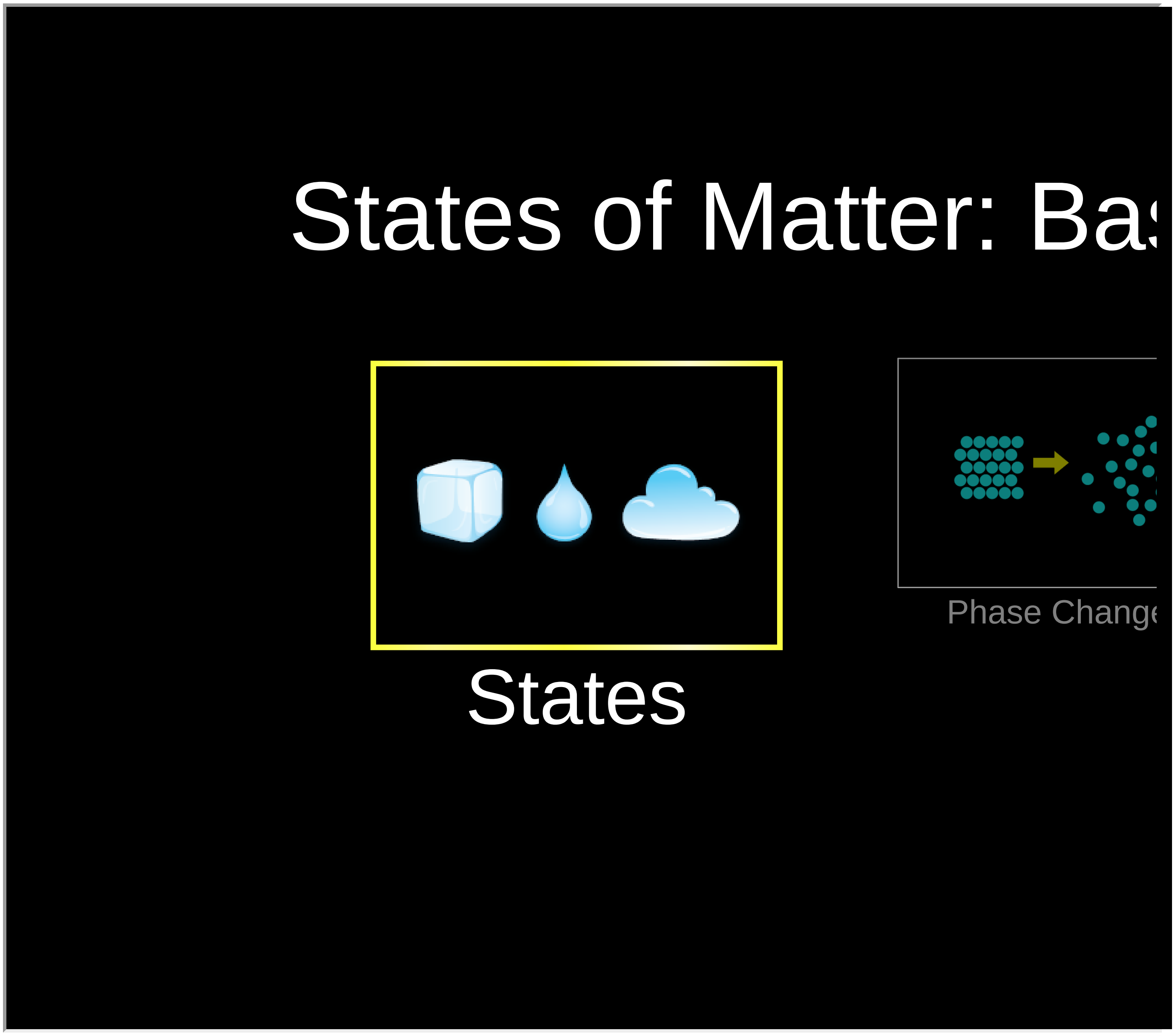
(a)

Cold water

(b)

Figure 2.8.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Two molecular drawings are shown and labeled a and b. Drawing a is a box containing fourteen red spheres that are surrounded by lines indicating that the particles are moving rapidly. This drawing has a label that reads “Hot water.” Drawing b depicts another box of equal size that also contains fourteen spheres, but these are blue. They are all surrounded by smaller lines that depict some particle motion, but not as much as in drawing a. This drawing has a label that reads “Cold water.”



States of Matter: Bas

States

Phase Chang

Measuring Energy and Heat Capacity

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{2.8.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0\ ^\circ\text{C}} = 363 \text{ J}/^\circ\text{C} \tag{2.8.2}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0\ ^\circ\text{C}} = 1814 \text{ J}/^\circ\text{C} \tag{2.8.3}$$

The specific heat capacity (c) of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{\text{m}\Delta\text{T}} \tag{2.8.4}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0\ ^\circ\text{C})} = 0.449 \text{ J/g }^\circ\text{C} \tag{2.8.5}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4,040 \text{ g})(50.0\ ^\circ\text{C})} = 0.449 \text{ J/g }^\circ\text{C} \tag{2.8.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 2.8.7).

Figure 2.8.7: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

The picture shows two black metal frying pans sitting on a flat surface. The left pan is about half the size of the right pan.

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 2.8.1.

Table 2.8.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$\begin{aligned} q &= (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change}) \\ q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned}$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example 2.8.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J}/\ \cancel{\text{g}}\,^\circ\text{C}) \times (800\ \ \cancel{\text{g}}) \times (85 - 21)^\circ\text{C} \\ &= (4.184\ \text{J}/\ \cancel{\text{g}}\,^\circ\ \cancel{\text{C}}) \times (800\ \ \cancel{\text{g}}) \times (64)^\circ\ \cancel{\text{C}} \\ &= 210,000\ \text{J} (= 210\ \text{kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 2.8.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.05×10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 2.8.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned}$$

Substituting the known values:

$$6,640\ \text{J} = c \times (348\ \text{g}) \times (43.6 - 22.4)\ ^\circ\text{C}$$

Solving:

$$c = \frac{6,640\ \text{J}}{(348\ \text{g}) \times (21.2^\circ\text{C})} = 0.900\ \text{J/g}\ ^\circ\text{C}$$

Comparing this value with the values in Table 2.8.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 2.8.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45\ \text{J/g}\ ^\circ\text{C}$; the metal is likely to be iron from checking Table 2.8.1

Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat “stored” in that substance is then converted into electricity.

The Solana Generating Station in Arizona’s Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 2.8.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

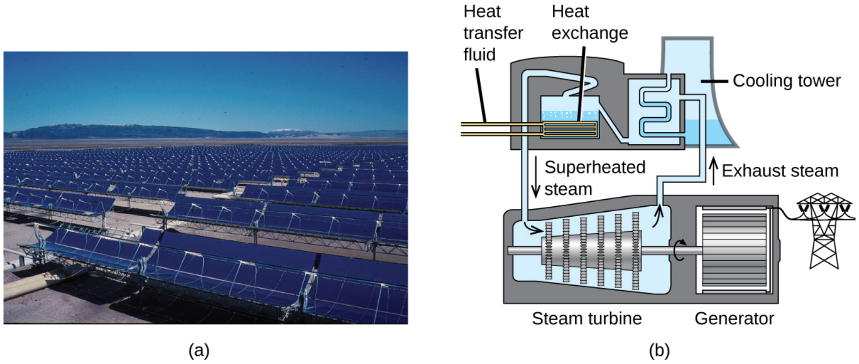
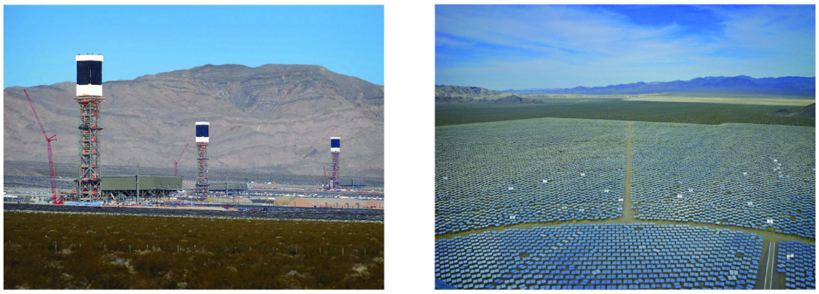


Figure 2.8.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

This figure has two parts labeled a and b. Part a shows rows and rows of trough mirrors. Part b shows how a solar thermal plant works. Heat transfer fluid enters a tank via pipes. The tank contains water which is heated. As the heat is exchanged from the pipes to the water, the water becomes steam. The steam travels to a steam turbine. The steam turbine begins to turn which powers a generator. Exhaust steam exits the steam turbine and enters a cooling tower.

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 2.8.9). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a) (b)

Figure 2.8.9: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

Two pictures are shown and labeled a and b. Picture a shows a thermal plant with three tall metal towers. Picture b is an arial picture of the mirrors used at the plant. They are arranged in rows.

Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics). Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J). Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Glossary

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat (*q*)

transfer of thermal energy between two bodies

heat capacity (*C*)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

kinetic energy

energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (c)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (w)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

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2.9: Measuring Heat

As the idea of heat as a form of transferring energy was first being developed, a unit amount of heat was taken to be the amount that was needed to increase the temperature of a reference material by one degree. Water was the reference material of choice, and the calorie was defined as the quantity of heat that raised the temperature of one gram of water one degree kelvin. The amount of heat exchanged by a known amount of water could then be calculated from the amount by which the temperature of the water changed. If, for example, introducing 63.55 g (1 mole) of copper metal, initially at 274.0 K, into 100 g of water, initially at 373.0 K, resulted in thermal equilibrium at 288.5 K, the water surrendered

$$100\ \text{ g } \times 1 \text{ cal g}^{-1}\text{ K}^{-1} \times 84.5 \text{ K} = 8450 \text{ cal}$$

This amount of heat was taken up by the copper, so that 0.092 cal was required to increase the temperature of one gram of copper by one degree K. Given this information, the amount of heat gained or lost by a known mass of copper in any subsequent experiment can be calculated from the change in its temperature.

Joule developed the idea that mechanical work can be converted entirely into heat. The quantity of heat that could be produced from one unit of mechanical work was called the ***mechanical equivalent of heat***. Today we ***define*** the unit of heat in mechanical units. That is, we define the unit of energy, the joule (J), in terms of the mechanical units mass (kg), distance (m), and time (s). One joule is one newton-meter or one $\text{kg m}^2\text{ s}^{-2}$. ***One calorie is now defined as*** $\mathbf{4.184\ J}$***, exactly.*** This definition assumes that heat and work are both forms of energy. This assumption is an intrinsic element of the first law of thermodynamics. This aspect of the first law is, of course, just a restatement of Joule's original idea.

When we want to measure the heat added to a system, measuring the temperature increase that occurs is often the most convenient method. If we know the temperature increase in the system, and we know the temperature increase that accompanies the addition of one unit of heat, we can calculate the heat input to the system. Evidently, it is useful to know how much the temperature increases when one unit of heat is added to various substances. Let us consider a general procedure for accumulating such information.

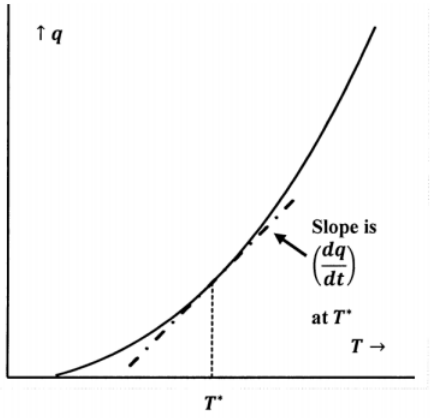

Figure 5. Heat capacity is the slope of q *versus* T.

First, we need to choose some standard amount of the substance in question. After all, if we double the amount, it takes twice as much heat to effect the same temperature change. One mole is a natural choice for this standard amount. If we add small increments of heat to one mole of a pure substance, we can measure the temperature after each addition and plot heat *versus* temperature. Figure 5 shows such a plot. (In experiments like this, it is often convenient to introduce the heat by passing a known electrical current, I, through a known resistance, R, immersed in the substance. The rate at which heat is produced is I^2R. Except for the usually negligible amount that goes into warming the resistor, all of it is transferred to the substance.) At any particular temperature, the slope of the graph is the increment of heat input divided by the incremental temperature increase. This slope is so useful, it is given a name; it is the molar heat capacity of the substance, C. Since this slope is also the derivative of the q-*versus*-T curve, we have

$$C = \frac{dq}{dT}$$

The temperature increase accompanying a given heat input varies with the particular conditions under which the experiment is done. In particular, the temperature increase will be less if some of the added heat is converted to work, as is the case if the volume of the system increases. If the volume increases, the system does work on the surroundings. For a given q, ΔT will be less when the system is allowed to expand, which means that $q/\Delta T$ will be greater. Heat capacity measurements are most conveniently done with the system at a constant pressure. However, the heat capacity at constant volume plays an important role in our theoretical development. The heat capacity is denoted C_P when the pressure is constant and C_V when the volume is constant. We have the important definitions

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

and

$$C_V = \left(\frac{\partial q}{\partial T} \right)_V$$

Since no pressure–volume work can be done when the volume is constant, less heat is required to effect a given temperature change, and we have $C_P > C_V$, as a general result. (In §14, we consider this point further.) If the system contains a gas, the effect of the volume increase can be substantial. For a monatomic ideal gas, the temperature increase at constant pressure is only 60% of the temperature increase at constant volume for the same input of heat.

2.10: Temperature Dependence of Enthalpy

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

At constant pressure

$$dH = C_p \, dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_2}^{T_2} C_p \, dT \tag{2.10.1}$$

Equation 2.10.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p \, \Delta T \tag{2.10.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 2.10.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{2.10.3}$$

After combining Equations 2.10.3 and 2.10.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) dT \tag{2.10.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2} T^2 - \frac{c}{T} \right]_{T_1}^{T_2} \tag{2.10.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{2.10.6}$$

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

Table 2.10.1: *Empirical Parameters for the temperature dependence of* C_p

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

✓ Example 2.10.1: Heating Lead

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

Solution

The enthalpy change is given by Equation 2.10.1 with a temperature dependence C_p given by Equation 2.10.1 using the parameters in Table 2.10.1. This results in the integral form (Equation 2.10.6):

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

when substituted with the relevant parameters of Pb(s) from Table 2.10.1.

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

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

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

✓ Example 2.10.2: Enthalpy of Formation

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

Solution

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

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

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

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

2.11: The Joule-Thomson Effect

In 1852, working with William Thomson (who would later become Lord Kelvin), Joule conducted an experiment in which they pumped gas at a steady rate through a lead pipe that was cinched to create a construction. On the upstream side of the constriction, the gas was at a higher pressure than on the downstream side of the constriction. Also, the temperature of the gas was carefully monitored on either side of the construction. The cooling that they observed as the gas expanded from a high pressure region to a lower pressure region was extremely important and lead to a common design of modern refrigerators.

Not all gases undergo a cooling effect upon expansion. Some gases, such as hydrogen and helium, will experience a warming effect upon expansion under conditions near room temperature and pressure. The direction of temperature change can be determined by measuring the Joule-Thomson coefficient, μ_{JT}. This coefficient has the definition

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H$$

Schematically, the Joule-Thomson coefficient can be measured by measuring the temperature drop or increase a gas undergoes for a given pressure drop (Figure $2.11.1$). The apparatus is insulated so that no heat can be transferred in or out, making the expansion isenthalpic.

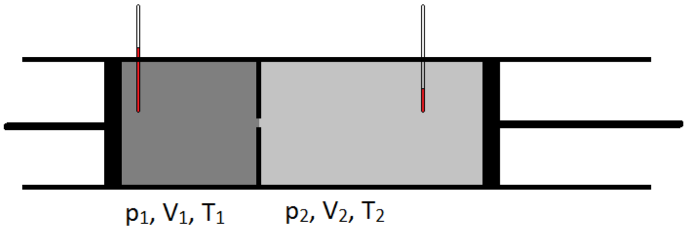

Figure 2.11.1:

The typical behavior of the Joule-Thomson coefficient can be summarized in Figure $2.11.2$. At the combinations of T and p for which $\mu_{JT} > 0$ (inside the shaded region), the sample will cool upon expansion. At those p and T conditions outside of the shaded region, where $\mu_{JT} < 0$, the gas will undergo a temperature increase upon expansion. And along the boundary, a gas will undergo neither a temperature increase not decrease upon expansion. For a given pressure, there are typically two temperatures at which μ_{JT} changes sign. These are the upper and lower inversion temperatures.

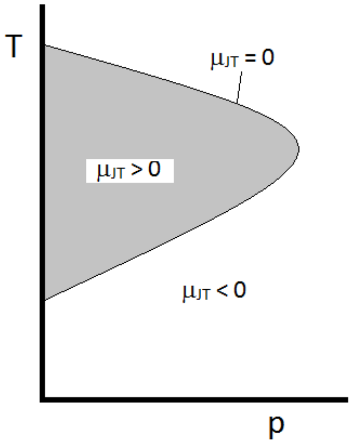

Figure 2.11.2: The typical behavior of the Joule-Thomson coefficient at different temperatures and pressures.

Using the tools of mathematics, it is possible to express the Joule-Thomson coefficient in terms of measurable properties. Consider enthalpy as a function of pressure and temperature: $H(p,T)$. This suggests that the total differential dH can be expressed

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \tag{2.11.1}$$

It will be shown later (again, once we develop the *Maxwell Relations*) that

$$\left(\frac{\partial H}{\partial p}\right)_T dp=-T\left(\frac{\partial V}{\partial T}\right)_p+V$$

A simple substitution shows

$$\left(\frac{\partial H}{\partial p}\right)_T dp=-TV\alpha+V=V(1-T\alpha)$$

So

$$dH=V(1-T\alpha)dP+C_p dT$$

For an ideal gas, $\alpha=1/T$, so

$$dH=\cancelto{0}{V\left(1-T\frac{1}{T}\right)dP}+C_p dT$$

which causes the first term to vanish. So for constant enthalpy expansion ($dH=0$), there can be no change in temperature ($dT=0$). This will mean that gases will only show non-zero values for μ_{JT} only because they deviate from ideal behavior!

✓ Example 2.11.1:

Derive an expression for μ_{JT} in terms of α, C_p, V, and T.

Solution

Using the total differential for $H(p,T)$ (Equation 2.11.1):

$$dH=\left(\frac{\partial H}{\partial p}\right)_T dp+\left(\frac{\partial H}{\partial T}\right)_p dT$$

Dividing by dp and constraining to constant H:

$$\left.\frac{dH}{dp}\right|_H=\left(\frac{\partial H}{\partial p}\right)_T\left.\frac{dp}{dp}\right|_H+\left(\frac{\partial H}{\partial T}\right)_p\left.\frac{dT}{dp}\right|_H$$

Noting that

$$\left.\frac{dH}{dp}\right|_H=0$$

$$\left.\frac{dp}{dp}\right|_H=1$$

and

$$\left.\frac{dT}{dp}\right|_H=\left(\frac{\partial T}{\partial p}\right)_H$$

so

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

We can then use the following substitutions:

$$\left(\frac{\partial H}{\partial p}\right)_T=V(1-T\alpha)$$

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

$$\left(\frac{\partial T}{\partial p}\right)_H = \mu_{JT}$$

To get

$$0 = V(1 - T\alpha) + C_p \mu_{JT}$$

And solving for μ_{JT} gives

$$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1)$$

2.12: Adiabatic Changes

The following discussions apply to a sample of ideal gas in an isolated system (an adiabatic, or thermally insulated system) that undergoes a reversible, adiabatic expansion or compression against a constant external pressure. Because there is no heat exchange during these volume changes, the internal energy will decrease during an expansion and increase during a compression. These internal energy changes occur because the gas molecules lose kinetic energy as they do work to move the piston, or gain kinetic energy as work is done on the by the piston.

Changes in Temperature

In this example, we want to find the change in temperature of a gas sample as it undergoes a reversible adiabatic expansion. This expansion will lead to a decrease in temperature and an increase in volume. It would be difficult to monitor the point-by-point changes in temperature as the volume slowly increases. However, because ΔU is a state function, we can separate the overall process into two theoretical steps:

- Step 1: an isothermal expansion from V_1 to V_2
- Step 2: a decrease in temperature at constant volume.

In Topic 2A we noted that the internal energy of an ideal gas is independent of the volume of its container. Because of this fact, the isothermal expansion in Step 1 will not affect the internal energy of the gas. Thus, the change in internal energy during the adiabatic expansion can be assigned to Step 2, the change in temperature at constant volume. Once again using a concept developed in Topic 2A, we know that at constant volume

$$\Delta U = C_V \, \Delta T = C_V \, (T_2 - T_1) \tag{2.12.1}$$

As noted above, in an adiabatic process $\Delta U = w_{ad}$ so that

$$w_{ad} = C_V \, \Delta T \tag{2.12.2}$$

This relationship makes sense because the energy needed to carry out the work of the expansion must come from the gas particles, which will lose energy as they do work, resulting in a drop in the temperature of the system.We assume that the value of C_V is independent of temperature.

To determine the relationship between the volume change and the temperature change, we can start with the premise that the work done by an ideal gas as it expands adiabatically against an external pressure, P, is

$$dw = -PdV \tag{2.12.3}$$

For an adiabatic change $dU = dw$ and for an ideal gas $dU = C_V dT$, thus in this case

$$dU = C_V dT = dw = -PdV \tag{2.12.4}$$

and

$$C_V dT = -PdV \tag{2.12.5}$$

Because we are using an ideal gas, $P = \dfrac{nRT}{V}$, thus

$$\frac{C_V dT}{T} = -\frac{nRdV}{V} \tag{2.12.6}$$

The limits of integration are set by the initial conditions (T_1, V_1) and final conditions (T_2, V_2):

$$C_V = \int \frac{dT}{T} = -nR \int \frac{dV}{V} \tag{2.12.7}$$

resulting in

$$C_V \ln \frac{T_2}{T1} = -nR \frac{V_2}{V_1} \tag{2.12.8}$$

which can be rearranged to

$$\frac{C_V}{nR} \ln \frac{T_2}{T_1} = \ln \frac{V_1}{V_2} \tag{2.12.9}$$

To solve for T_2, we need to define $\frac{C_V}{nR} = c$ so that

$$\ln \left(\frac{T_2}{T_1}\right)^c = \ln \frac{V_1}{V_2} \tag{2.12.10}$$

This equation allows us to assume that

$$\left(\frac{T_2}{T_1}\right)^c = \frac{V_1}{V_2} \tag{2.12.11}$$

and so

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{1/c} \tag{2.12.12}$$

Example 2.12.1:

Calculate the final temperature, the work done, and the change in internal energy when 0.0500 moles of He at 25.0°C undergoes a reversible adiabatic expansion from 250. L to 750. L. The constant volume molar heat capacity of He at 25°C is $12.48 \frac{J}{mole \cdot K}$.

Asked For: T_f, w_{ad}, and ΔU

Solution: If $C_V = 12.48 \frac{J}{mole \cdot K}$, then c = $\frac{12.48 \frac{J}{mole \cdot K}}{/} 8.314 \frac{J}{mole \cdot K}$ = 1.501.

Use equation 2.12.12to find that $T_2 = 298.15\, K \times \left(\frac{250.\, L}{750.\, L}\right)^{1/1.501} = 143\, K$.

Use equation 2.12.2to find that $w_{ad} = (0.0500\, moles\, He) \times \left(12.48 \frac{J}{mole \cdot K}\right) \times (143K - 298K) = -96.7\, J$.

According to the definition of an adiabatic process, $\Delta U = w_{ad}$. Therefore, ΔU = -96.7 J.

Exercise 2.12.1

Calculate the final temperature, the work done, and the change in internal energy when 0.0400 moles of CO at 25.0°C undergoes a reversible adiabatic expansion from 200. L to 800. L. The constant volume molar heat capacity of CO at 25°C is $20.16 \frac{J}{mole \cdot K}$.

Answers: T_f = 168 K; w_{ad} = -105 J; ΔU = - 105 J

Changes in Pressure

In this example, we want to find the change in pressure of a gas sample as it undergoes a reversible adiabatic expansion. This expansion will lead to a decrease in pressure and an increase in volume. Because we are working with an ideal gas

$$\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2} \tag{2.12.13}$$

Substituting in a rearranged version of Equation 2.12.12, we get

$$\frac{P_1 V_1}{P_2 V_2} = \left(\frac{V_2}{V_1}\right)^{\frac{1}{c}} \tag{2.12.14}$$

which rearranges to

$$\frac{P_1}{P_2}\left(\frac{V_1}{V_2}\right)^{\frac{1}{c}+1} = 1 \tag{2.12.15}$$

In Topic 2B, it was stated that $C_{P,m} - C_{V,m} = R$. This relationship can be used to develop the term, γ:

$$\frac{1}{c} + 1 = \frac{1+c}{c} = \frac{R + C_{V,m}}{C_{V,m}} = \frac{C_{P,m}}{C_{V,m}} = \gamma \tag{2.12.16}$$

Thus, Equation 2.12.15can be written as

$$\frac{P_1}{P_2}\left(\frac{V_1}{V_2}\right)^{\gamma} = 1 \tag{2.12.17}$$

Solving for P_2, we get

$$P_2 = P_1 \times \left(\frac{V_1}{V_2}\right)^{\gamma} \tag{2.12.18}$$

recall that:

- for a monatomic ideal gas, $C_{V,m} = \frac{3}{2}R$ and $C_{P,m} = \frac{5}{2}R$, so $\gamma = \frac{5}{3}$.
- for nonlinear, polyatomic molecules, which can rotate as well as translate, $C_{V,m} = 3R$ and $C_{P,m} = 4R$, so $\gamma = \frac{4}{3}$.

Example 2.12.2:

Calculate the final pressure when a sample of He at 250. kPa undergoes a reversible adiabatic expansion from 2.00 L to 4.00 L.

Solution: Use equation 2.12.18and the fact that $\gamma = \frac{5}{3}$ for He to find that $P_f = (250kPa)\left(\frac{2.00\ L}{4.00\ L}\right)^{5/3} = 78.7kPa$.

Exercise 2.12.2

Calculate the final pressure when a sample of Xe at 100. kPa undergoes a reversible adiabatic expansion from 1.00 L to 5.00 L.

Answer $P_f = 6.84kPa$.

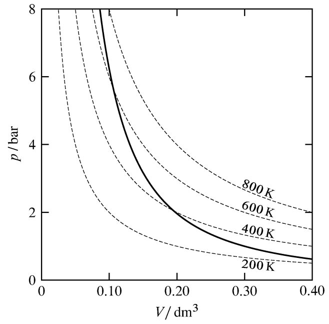

***Figure 2.5.1** An adiabat (solid curve) and four isotherms (dashed curves) for an ideal gas ($n = 0.0120$ mole, ($CV_m = 1.5R$). Image by Howard DeVoe.*

The solid curve in Fig. 2.5.1 shows how the pressure of an ideal gas varies with volume during a reversible adiabatic expansion or compression. This curve is an *adiabat*. The dashed curves in the figure are *isotherms* showing how pressure changes with volume at constant temperature according to the equation of state $p = nRT/V$. In the direction of increasing V (expansion), the adiabat crosses isotherms of progressively lower temperatures. This cooling effect, of course, is due to the loss of energy by the gas as it does work on the surroundings without a compensating flow of heat into the system.

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CHAPTER OVERVIEW

3: Entropy and the Second and Third Laws

3.1: Energy Does not Determine Spontaneity

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

Not so:

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

Clearly the first law is not enough to describe nature.

3.1.1: Two items left on our wish list

The development of the new state function entropy has brought us much closer to a complete understanding of how heat and work are related:

1. the spontaneity problem

   we now have a criterion for spontaneity for isolated systems

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

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

Two problems remain:

1. we would like a spontaneity criterion *for all systems* (not just isolated ones)
2. we have a new state function S, but what is it?

3.1.2: Entropy on a microscopic scale

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

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

3.1.2.1: Permutations

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

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

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

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

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

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

Causality vs. Correlation

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

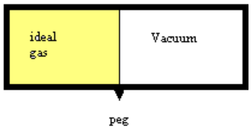
An adult White Stork. from Wikipedia (credit: Frank Vassen).

Answer:

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

3.1.3: Changing the size of the box with the particles in it

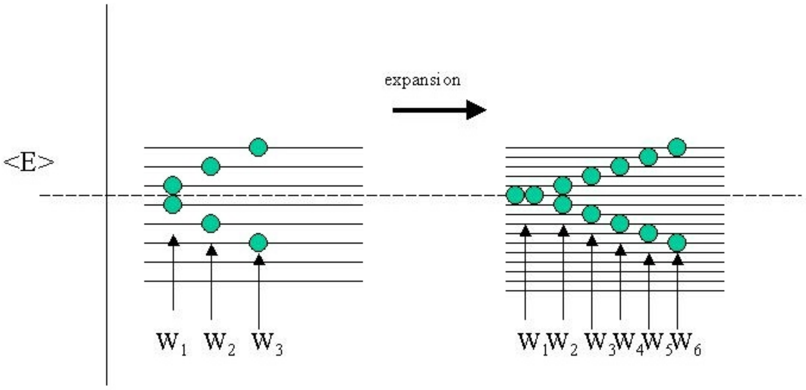
The expansion of an ideal gas against vacuum is really a wonderful *model experiment*, because *nothing else happens* but a spontaneous expansion and a change in entropy. No energy change, no heat, no work, no change in mass, no interactions, nothing. In fact, it does not even matter whether we consider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



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

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

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



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

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

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

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

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

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

$$S = k \ln W$$

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

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

3.2: Introduction to the Second Law

Rudolph Clausius is kind enough in his 1879 work “The Mechanical Theory of Heat” (Clausius, 1879) to indicate where we have been in our discussion of thermodynamics, as well as where we are going.

> “The fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat:
> 1. The energy of the universe is constant.
> 2. The entropy of the universe tends to a maximum.”
> — Rudolf Clausius, The Mechanical Theory Of Heat

The **second law of thermodynamics**, which introduces us to the topic of entropy, is amazing in how it constrains what we can experience and what we can do in the universe. As Sean M. Carroll, a CalTech Theoretical physicist, suggests in a 2010 interview with Wired Magazine (Biba, 2010),

> *I’m trying to understand how time works. And that’s a huge question that has lots of different aspects to it. A lot of them go back to Einstein and spacetime and how we measure time using clocks. But the particular aspect of time that I’m interested in is the arrow of time: the fact that the past is different from the future. We remember the past but we don’t remember the future. There are irreversible processes. There are things that happen, like you turn an egg into an omelet, but you can’t turn an omelet into an egg.*

We, as observers of nature, are time travelers. And the constraints on what we can observe as we move through time step from the **second law of thermodynamics**. But more than just understanding what the second law says, we are interested in what sorts of processes are possible. And even more to the point, what sorts of processes are **spontaneous**.

A spontaneous process is one that will occur without external forces pushing it. A process can be spontaneous even if it happens very slowly. Unfortunately, Thermodynamics is silent on the topic of how fast processes will occur, but is provides us with a powerful toolbox for predicting which processes will be spontaneous. But in order to make these predictions, a new thermodynamic law and variable is needed since the first law (which defined ΔU and ΔH) is insufficient.

Consider the following processes:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

with $\Delta H < 0$

$$NaHCO_3(s) \rightarrow Na+(aq) + HCO_3^-(aq)$$

with $\Delta H > 0$

Both reactions will occur spontaneously, but one is exothermic and the other endothermic. So while it is intuitive to think that an exothermic process will be spontaneous, there is clearly more to the picture than simply the release of energy as heat when it comes to making a process spontaneous. The Carnot cycle because a useful thought experiment to explore to help to answer the question of why a process is spontaneous.

Contributors

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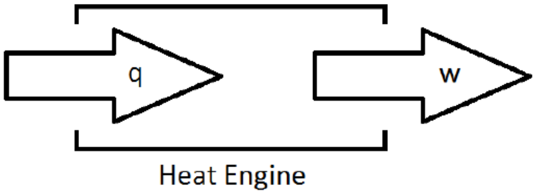
3.3: Heat Engines and the Carnot Cycle

Heat Engines

Sadi Carnot (1796 – 1832) (Mendoza, 2016), a French physicist and engineer was very interested in the improvement of steam engines to perform the tasks needed by modern society.

Figure 3.3.1: Sadi Carnot (1796 - 1832)

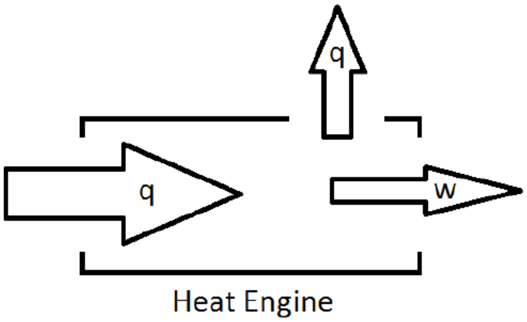
To simplify his analysis of the inner workings of an engine, Carnot devised a useful construct for examining what affect engine efficiency. His construct is the **heat engine**. The idea behind a heat engine is that it will take energy in the form of heat, and transform it into an equivalent amount of work.



Unfortunately, such a device is impractical. As it turns out, nature prevents the complete conversion of energy into work with perfect efficiency. This leads to an important statement of the **Second Law of Thermodynamics**.

> *It is impossible to convert heat into an equivalent amount of work without some other changes occurring in the universe.*

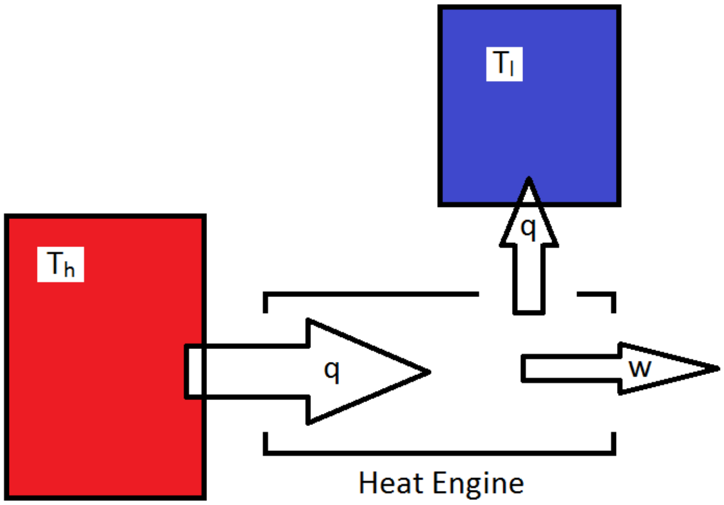
As such, a more reasonable picture of the heat engine is one which will allow for losses of energy to the surroundings.



The fraction of energy supplied to the engine that can be converted to work defines the efficiency of the engine.

The Carnot Cycle

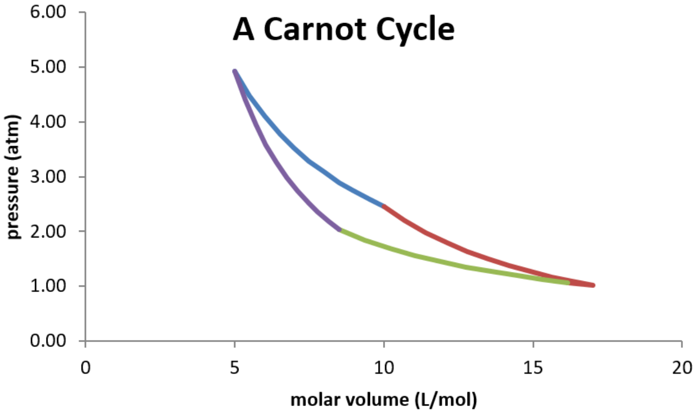
The Carnot cycle is a theoretical cyclic heat engine that can used to examine what is possible for an engine for which the job is convert heat into work. For simplicity, all energy provided to the engine occurs isothermally (and reversibly) at a temperature T_h and all of the energy lost to the surroundings also occurs isothermally and reversibly at temperature T_l. In order to insure this, the system must change between the two temperatures adiabatically.



Thus, the cycle consists of four reversible legs, two of which are isothermal, and two of which are adiabatic.

I. Isothermal expansion from p_1 and V_1 to p_2 and V_2 at T_h.
II. Adiabatic expansion from p_2, V_2, T_h to p_3, V_3, T_l.
III. Isothermal compression from p_3 and V_3 to p_4 and V_4 at T_l.
IV. Adiabatic compression from p_4, V_4, T_l to p_1, V_1, T_h.

Plotted on a pressure-volume diagram, the Carnot cycle looks as follows:



Because this is a closed cycle (the ending state is identical initial state) any state function must have a net change of zero as the system moves around the cycle. Furthermore, the efficiency of the engine can be expressed by the net amount of work the engine produces per unit of heat supplied to power the engine.

$$\epsilon = \frac{w_{net}}{q_h}$$

In order to examine this expression, it is useful to write down expressions fo the heat and work flow in each of the four legs of the engine cycle.

Leg	Heat	Work
I	$q_h = -nRT_h \ln(V_2/V_1)$	$nRT_h \ln(V_2/V_1)$
II	0	$C_V(T_l - T_h)$
III	$q_l = -nRT_l \ln(V_4/V_3)$	$nRT_l \ln(V_4/V_3)$
IV	0	$C_V(T_h - T_l)$

The total amount of work done is given by the sum of terms in the thirst column. Clearly the terms for the two adiabatic legs cancel (as they have the same magnitude, but opposite signs.) So the total work done is given by

$$w_{tot} = nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

The efficiency of the engine can be defined as the total work produced per unit of energy provided by the high temperature reservoir.

$$\epsilon = \frac{w_{tot}}{q_h}$$

or

$$\epsilon = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)} \tag{3.3.1}$$

That expression has a lot of variables, but it turns out that it can be simplified dramatically. It turns out that by the choice of pathways connecting the states places a very important restriction on the relative values of V_1, V_2, V_3 and V_4. To understand this, we must consider how the work of adiabatic expansion is related to the initial and final temperatures and volumes. In Chapter 3, it was shown that the initial and final temperatures and volumes of an adiabatic expansion are related by

$$V_i T_i^{C_V/R} = V_f T_f^{C_V/R}$$

or

$$\frac{V_i}{V_f} = \left(\frac{T_f}{T_i}\right)^{C_V/R}$$

Using the adiabatic expansion and compression legs (II and IV), this requires that

$$\frac{V_2}{V_2} = \left(\frac{T_h}{T_l}\right)^{C_V/R}$$

and

$$\frac{V_4}{V_1} = \left(\frac{T_l}{T_h}\right)^{C_V/R}$$

Since the second terms are reciprocals of one another, the first terms must be as well!

$$\frac{V_2}{V_2} = \frac{V_1}{V_4}$$

A simple rearrangement shows that

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

This is very convenient! It is what allows for the simplification of the efficiency expression (Equation 3.3.1) becomes

$$\epsilon = \frac{n\cancel{R}T_h \ln \cancel{\left(\frac{V_2}{V_1}\right)} + n\cancel{R}T_l \ln \cancel{\left(\frac{V_2}{V_1}\right)}}{n\cancel{R}T_h \ln \cancel{\left(\frac{V_2}{V_1}\right)}}$$

Canceling terms in the numerator and denominator yields

$$\epsilon = \frac{T_g - T_l}{T_h} \tag{3.3.2}$$

This expression gives the maximum efficiency and depends only on the high and low temperatures!

Also, it should be noted that the heat engine can be run backwards. By providing work to the engine, it can be forces to draw heat from the low temperature reservoir and dissipate it into the high temperature reservoir. This is how a refrigerator or heat pump works. The limiting efficiency of such a device can also be calculated using the temperatures of the hot can cold reservoirs.

✓ Example 3.3.1:

What is the maximum efficiency of a freezer set to keep ice cream at a cool -10 ^{o}C, which it is operating in a room that is 25^{o}C? What is the minimum amount of energy needed to remove 1.0 J from the freezer and dissipate it into the room?

Solution

The efficiency is given by Equation 3.3.2 and converting the temperatures to an absolute scale, the efficiency can be calculated as

$$\epsilon = \frac{298\ K - 263\ K}{298\ K}$$

This value can be used in the following manner

$$energy_{transferred} = \epsilon(work_{required})$$

So

$$1.0\ J = 0.1174(w)$$

or

$$w = 8.5\ J$$

It is interesting to note that any arbitrary closed cyclical process can be described as a sum of infinitesimally small Carnot cycles, and so all of the conclusions reached for the Carnot cycle apply to any cyclical process.

Contributors

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3.4: Entropy

In addition to learning that the efficiency of a Carnot engine depends only on the high and low temperatures, more interesting things can be derived through the exploration of this system. For example, consider the total heat transferred in the cycle:

$$q_{tot} = nRT_h \ln\left(\frac{V_2}{V_1}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

Making the substitution

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

the total heat flow can be seen to be given by

$$q_{tot} = nRT_h \ln\left(\frac{V_4}{V_3}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

It is clear that the two terms do not have the same magnitude, unless $T_h = T_l$. This is sufficient to show that q is **not a state function**, since it's net change around a closed cycle is not zero (as any value of a state function must be.) However, consider what happens when the sum of q/T is considered:

$$\begin{aligned} \sum \frac{q}{T} &= \frac{nR\,\cancel{T_h} \ln\left(\frac{V_4}{V_3}\right)}{\cancel{T_h}} - \frac{nR\,\cancel{T_l} \ln\left(\frac{V_4}{V_3}\right)}{\cancel{T_l}} \\ &= nR \ln\left(\frac{V_4}{V_3}\right) - nR \ln\left(\frac{V_4}{V_3}\right) \\ &= 0 \end{aligned}$$

This is the behavior expected for a state function! It leads to the definition of entropy in differential form,

$$dS \equiv \frac{dq_{rev}}{T}$$

In general, dq_{rev} will be larger than dq (since the reversible pathway defines the maximum heat flow.) So, it is easy to calculate entropy changes, as one needs only to define a reversible pathway that connects the initial and final states, and then integrate dq/T over that pathway. And since \(\Delta S\) is defined using q for a reversible pathway, ΔS is *independent* of the actual path a system follows to undergo a change.

Contributors and Attributions

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

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

$$dU = C_v dT$$

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

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

This means that we can write:

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

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

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

And the following would be true:

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

From our equation above, we know that:

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

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

Therefore, the following should be true:

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

However,

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

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

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

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

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

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

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

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

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

3.6: Calculating Entropy Changes

Entropy changes are fairly easy to calculate so long as one knows initial and final state. For example, if the initial and final volume are the same, the entropy can be calculated by assuming a reversible, isochoric pathway and determining an expression for $\frac{dq}{T}$. That term can then be integrated from the initial condition to the final conditions to determine the entropy change.

Isothermal Changes

If the initial and final temperatures are the same, the most convenient reversible path to use to calculate the entropy is an isothermal pathway. As an example, consider the isothermal expansion of an ideal gas from V_1 to V_2. As was derived in Chapter 3,

$$dq = nRT\frac{dV}{V}$$

So dq/T is given by

$$\frac{dq}{T} = nR\frac{dV}{V}$$

and so

$$\Delta S = \int \frac{dq}{T} = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR\ln\left(\frac{V_2}{V_1}\right) \tag{3.6.1}$$

✓ Example 3.6.1: Entropy Change for a Gas Expansion

Calculate the entropy change for 1.00 mol of an ideal gas expanding isothermally from a volume of 24.4 L to 48.8 L.

Solution

Recognizing that this is an isothermal process, we can use Equation 3.6.1

$$\begin{aligned}\Delta S &= nR\ln\left(\frac{V_2}{V_1}\right)\\ &= (1.00\, mol)(8.314 J/(mol\, K))\ln\left(\frac{44.8\, L}{22.4\, L}\right)\\ &= 5.76\, J/K\end{aligned}$$

Isobaric Changes

For changes in which the initial and final pressures are the same, the most convenient pathway to use to calculate the entropy change is an isobaric pathway. In this case, it is useful to remember that

$$dq = nC_p dT$$

So

$$\frac{dq}{T} = nC_p\frac{dT}{T}$$

Integration from the initial to final temperature is used to calculate the change in entropy. If the heat capacity is constant over the temperature range

$$\int_{T_1}^{T_2} \frac{dq}{T} = nC_p\int_{T_1}^{T_2} \frac{dT}{T} = nC_p\ln\left(\frac{T_2}{T_1}\right)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral. For example, if C_p can be expressed as

$$C_p = a + bT + \frac{c}{T^2}$$

ΔS takes the form

$$\int_{T_1}^{T_2} \frac{dq}{T} = n \int_{T_1}^{T_2} \frac{a + bT + \frac{c}{T^2}}{T} dT$$

which simplifies to

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a}{T} + bT + \frac{c}{T^3} \right) dT$$

or

$$\Delta S = n \left[a \ln\left(\frac{T_2}{T_1} \right) + b(T_2 - T_1) - \frac{c}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right) \right]$$

Isochoric Changes

Similarly to the cast of constant pressure, it is fairly simple to calculate ΔS. Since

$$dq = nC_V dt$$

$\frac{dq}{T}$ is given by

$$\frac{dq}{T} = nC_V \frac{dT}{T}$$

And so for changes over which C_V is independent of the temperature ΔS is given by

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1} \right)$$

Adiabatic Changes

The easiest pathway for which to calculate entropy changes is an adiabatic pathway. Since $dq = 0$ for an adiabatic change, then $dS = 0$ as well.

Phase Changes

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T} \tag{3.6.2}$$

✓ Example 3.6.2: Entropy Change for Melting Ice

The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.

Solution

This is a phase transition at constant pressure (assumed) requiring Equation 3.6.2:

$$\begin{aligned} \Delta S &= \frac{(1\, mol)(6010\, J/mol)}{273\, K} \\ &= 22\, J/K \end{aligned}$$

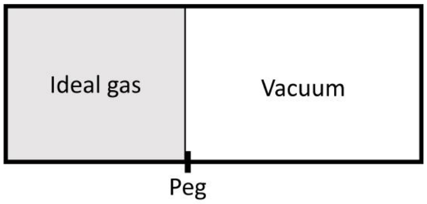
3.7: We Must Always Devise a Reversible Process to Calculate Entropy Changes

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

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

3.7.1: Vacuum Expansion

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



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

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

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

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

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

$$q_{rev} = nRT\ln\left(\frac{V_2}{V_1}\right) \tag{3.7.1}$$

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

$$\Delta S = \frac{q_{rev}}{T} \tag{3.7.2}$$

Substituting Equation 3.7.1 into Equation 3.7.2 results in

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

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

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

For the irreversible expansion into vacuum we see that

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

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

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

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

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

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

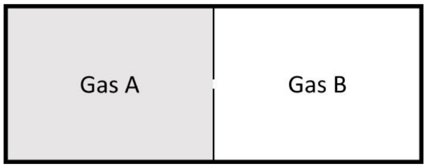
$$dS = \frac{\delta q}{T} \tag{3.7.3}$$

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

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

3.7.2: The Mixing of Two Gases

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



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

For gas A we can write:

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

and similarly for gas B we can write:

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

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

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

and the entropy change total per mole of gas is:

$$\frac{\Delta S}{n_{tot}} = R\frac{\left[n_B \ln \frac{n_{tot}}{n_B} + n_A \ln \frac{n_{tot}}{n_A}\right]}{n_{tot}} \tag{3.7.4}$$

Equation 3.7.4 can be simplified using mole fractions:

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

and the mathematical relationship of logarithms that:

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

to:

$$\Delta \bar{S} = -R\left[\chi_A \ln \chi_A + \chi_B \ln \chi_B\right] \tag{3.7.5}$$

In the case of mixing of more than two gases, Equation 3.7.5 can be expressed as:

$$\Delta \bar{S} = -R\sum \chi_i \ln \chi_i \tag{3.7.6}$$

This entropy expressed in Equations 3.7.5 and 3.7.6 is known as the **entropy of mixing**; its existence is the major reason why there is such a thing as diffusion and mixing when gases, and also solutions (even solid ones), are brought into contact with each other.

3.8: Comparing the System and the Surroundings

It is oftentimes important (for reasons that will be discussed in the next section) to calculate both the entropy change of the system as well as that of the surroundings. Depending on the size of the surroundings, they can provide or absorb as much heat as is needed for a process without changing temperature. As such, it is oftentimes a very good approximation to consider the changes to the surroundings as happening isothermally, even though it may not be the case for the system (which is generally smaller.)

✓ Example 3.8.1

Consider 18.02 g (1.00 mol) of ice melting at 273 K in a room that is 298 K. Calculate DS for the ice, the surrounding room, and of the universe. (DH_{fus} = 6.01 kJ/mol)

Solution

For the process under constant pressure: $q_{ice} = -q_{room}$:

$$q = n\Delta H_{fus} = (1.00\, mol)(6010\ J/mol) = 6010\ J$$

For the ice:

$$\Delta S_{ice} = \frac{q_{ice}}{T_{ice}} = \frac{6010\ J}{273\ K} = 22.0\ J/K$$

For the room:

$$\Delta S_{room} = \frac{q_{room}}{T_{room}} = \frac{-6010\ J}{298\ K} = -20.2\ J/K$$

For the universe:

$$\begin{aligned} \Delta S_{univ} &= \Delta S_{ice} + \Delta S_{room} \\ &= 22.0 J/K - 20.2\ J/K = 1.8\ J/K \end{aligned}$$

Note: ΔS_{univ} is positive, which is characteristic of a spontaneous change!

✓ Example 3.8.2

A 10.0 g piece of metal (C = 0.250 J/g °C) initially at 95 °C is placed in 25.0 g of water initially at 15 °C in an insulated container. Calculate the final temperature of the metal and water once the system has reached thermal equilibrium. Also, calculate the entropy change for the metal, the water, and the entire system.

Solution

Heat will be transferred from the hot metal to the cold water. Since it has nowhere else to go, the final temperature can be calculated from the expression

$$q_w = -q_m$$

where q_w is the heat absorbed by the water, and q_m is the heat lost by the metal. And since

$$q = mC\Delta T$$

it follows that

$$(25\ g)(4.184\ J/g\ ^\circ C))(T_f - 15\ ^\circ C) = -(10.0\ g)(0.250\ J/g\ ^\circ C))(T_f - 95\ J/g\ ^\circ C)$$

A bit of algebra determines the final temperature to be:

$$T_f = 16.9\ ^\circ C.$$

To get the entropy changes, use the expression:

$$\Delta S = mC_p \ln\left(\frac{T_f}{T_i}\right)$$

So, for the water:

$$\begin{aligned}\Delta S_{water} &= (25\,g)(4.184\,J/g\,^{\circ}C))\ln\left(\frac{289.9\,K}{288\,K}\right) \\ &= 0.689\,J/K\end{aligned}$$

And for the metal:

$$\begin{aligned}\Delta S_{metal} &= (10.0\,g)(0.250\,J/g\,^{\circ}C))\ln\left(\frac{289.9\,K}{368\,K}\right) \\ &= -0.596\,J/K\end{aligned}$$

For the system:

$$\begin{aligned}\Delta S_{sys} &= \Delta S_{water} + \Delta S_{metal} \\ &= 0.689\,J/K + -0.596\,J/K = 0.093\,J/K\end{aligned}$$

Note: The total entropy change is positive, suggesting that this will be a spontaneous process. This should make some sense since one expects heat to flow from the hot metal to the cool water rather than the other way around. Also, note that the sign of the entropy change is positive for the part of the system that is absorbing the heat, and negative for the part losing the heat.

In summary, ΔS can be calculated for a number of pathways fairly conveniently.

Table 3.8.1*: Summary of different ways to calculate ΔS depending on the pathway.*

Pathway	$\boldsymbol{\Delta S_{sys} = \ln \frac{dQ_{rev}}{T_{sys}}}$	$\boldsymbol{\Delta S_{surr} = \frac{q_{sys}}{T_{surr}}}$
Adiabatic	0	$\Delta S_{surr} = \frac{q_{sys}}{T_{surr}}$
Isothermal	$\frac{q_{rev}}{T}$ and $nR\ln\left(\frac{V_2}{V_1}\right)$ *	
Isobaric	$mC_p\ln\left(\frac{T_f}{T_i}\right)$	
Isochoric	$mC_V\ln\left(\frac{T_f}{T_i}\right)$	
Phase Change	$\frac{\Delta H_{phase}}{T}$	
**for an ideal gas.*		

And

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}.$$

This calculation is important as ΔS_{univ} provides the criterion for spontaneity for which we were searching from the outset. This also suggests a new way to state the second law:

> *The entropy of the universe increases in any spontaneous change.*

If we think of “the direction of spontaneous” to be the natural direction of chance, we can see that entropy and the second law are tied inexorably with the natural direction of the flow of time. Basically, we can expect the entropy of the universe to continue to increase as time flows into the future. We can overcome this natural tendency to greater entropy by doing work on a system. This is why it requires such great effort, for example, to straighten a messy desk, but little effort for the desk to get messy over time.

Clausius Inequality

The Second Law can be summed up in a very simple mathematical expression called the *Clausius Inequality*.

$$\Delta S_{universe} \geq 0$$

which must be true for any spontaneous process. It is not the most convenient criterion for spontaneity, but it will do for now. In the next chapter, we will derive a criterion which is more useful to us as chemists, who would rather focus on the system itself rather than both the system and its surroundings. Another statement of the Clausius theorem is

$$\oint \frac{dq}{T} \geq 0$$

with the only condition of the left hand side equaling zero is if the system transfers all heat reversibly.

Contributors

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3.9: Heat Capacity as a Function of Temperature

It is relatively easy to measure heat capacities as a function of temperature. If we measure the constant-pressure heat capacity of a pure substance over a wide temperature range, we typically observe a curve like that in Figure 1. The heat capacity is a smooth, continuous function of temperature except for a small number of discontinuities. These occur at temperatures where the substance undergoes phase changes. These can be changes from one solid phase to another, melting to convert a solid phase to the liquid, or vaporization to convert the liquid to the gas. The details of the curve are pressure dependent; for example, at a low pressure, we might observe sublimation of the material from a solid phase directly into its gas phase.

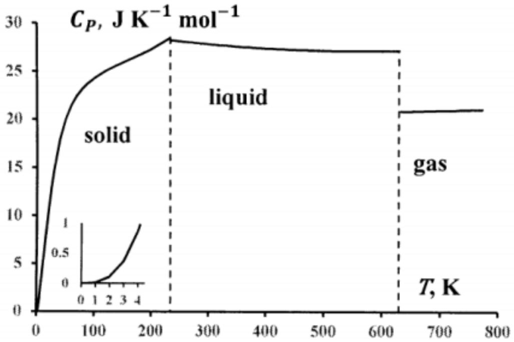

Figure 1. Heat capacity of mercury *versus* temperature

Another general feature of these curves is that the heat capacity of the solid substance decreases to zero as the absolute temperature decreases to zero; the curve meets the abscissa at the zero of temperature and does so asymptotically. That this is true for all substances seems like an odd sort of coincidence. Why should all solid substances exhibit essentially the same heat capacity (zero) at one temperature (absolute zero)?

As it turns out, this result has a straightforward molecular interpretation in the theory of statistical thermodynamics. In Section 22.6, we consider a theory of low-temperature heat capacity developed by Einstein. Einstein's theory explains all of the qualitative features that are observed when we measure heat capacities at low temperatures, but its predictions are not quantitatively exact. Debye extended the Einstein model and developed a theory that gives generally excellent quantitative predictions. The Debye theory predicts that, at temperatures near absolute zero, the heat capacity varies as the cube of temperature: $C_P = AT^3$, where A is a constant. If we have heat capacity data down to a temperature near absolute zero, we can estimate the value of A from the value of C_P at the lowest available temperature.

Anticipating results that we develop in Chapter 22, we can characterize the statistical interpretation as follows: When a system of molecules gives up heat to its surroundings, some of the molecules move from higher energy levels to lower ones. Statistical thermodynamics posits that the fraction of the molecules that are in the lowest energy level approaches one as the temperature goes to zero. If nearly all of the molecules are already in the lowest energy level, decreasing the temperature still further has a negligible effect on the energy and enthalpy of the system.

Given such heat capacity data, we can find the enthalpy or entropy change that occurs as we change the temperature of a quantity of the substance from some reference temperature to any other value. When we use pressure and temperature as the independent variables, we have

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

and

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

At constant pressure, we have

$$(dH)_P = C_P dT$$

so that

$$H\left(T\right)-H\left(T_{ref}\right)=\int^T_{T_{ref}}{C_PdT}$$

and

$$\left(dS\right)_P=\frac{C_P}{T}dT$$

so that

$$S\left(T\right)-S\left(T_{ref}\right)=\int^T_{T_{ref}}{\frac{C_P}{T}dT}$$

If phase transitions occur as the temperature goes from the reference temperature to the temperature of interest, these integrations must be carried out in steps. Also, we must include the enthalpy and entropy changes that occur during these phase changes.

3.10: The Third Law

For entropy on the other hand, the fact that the heat capacity goes to zero as the temperature decreases has important consequences. Consider the change in the entropy of a pure substance whose heat capacity approaches some finite limiting value as its temperature decreases to absolute zero. For such a substance, C_P/T becomes arbitrarily large as the temperature decreases, and the entropy integral

$$\int_T^0 \frac{C_P}{T}\,dT$$

approaches minus infinity as the temperature approaches zero. For real substances, this does not occur. In the neighborhood of absolute zero, heat capacities decrease more rapidly than temperature. The entropy change approaches zero as the temperature approaches zero.

The idea that the entropy change for a pure substance goes to zero as the temperature goes to zero finds expression as the third law of thermodynamics. In 1923, Lewis and Randall[1] gave a statement of the third law that is particularly convenient in chemical applications:

> *If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a positive finite entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.*

Implicitly, the Lewis and Randall statement defines the entropy of any substance, at any temperature, T, to be the difference between the entropy of the constituent elements, at absolute zero, and the entropy of the substance at temperature T. Equivalently, we can say that it is the entropy change when the substance is formed at temperature T from its constituent elements at absolute zero. Arbitrarily, but very conveniently, the statement sets the entropy of an element to zero at absolute zero.

The distinction between perfect crystalline substances and less-than-perfect crystalline substances lies in the regularity of the arrangement of the molecules within the crystal lattice. In any lattice, each molecule of the substance is localized at a specific site in the lattice. In a perfect crystal, all of the molecules are in oriented the same way with respect to the lattice. Some substances form crystals in which the molecules are not all oriented the same way. This can happen when the molecule can fit into a lattice site of the same shape in more than one way. For example, in solid carbon monoxide, the individual molecules occupy well-defined lattice sites. If the carbon monoxide crystal were perfect, all of the molecules would point in the same direction, as diagrammed in Figure 2. Instead, they point randomly in either of two possible directions.

Figure 2. A two-dimensional representation of a perfect CO crystal.

3.11: Absolute Entropy

By the Lewis and Randall statement of the third law, the entropy of a substance that forms a perfect crystal is identically equal to zero at absolute zero. Much as the ideal gas temperature scale has a natural zero at the temperature at which the volume extrapolates to zero, a perfect crystalline substance has a natural zero of entropy at this same temperature. We can choose a non-zero value for the absolute zero of temperature. The Centigrade scale is based on such a choice. However, for thermodynamic purposes, any such choice is much less convenient. Similarly, we could choose arbitrary values for the entropies of the elements at the absolute zero of temperature. The entropy of a perfect crystalline substance at absolute zero would then be the sum of the entropies of its constituent elements. (See problem 5.) However, choosing non-zero values proves to be much less convenient.

Given the entropy of a substance at absolute zero, its entropy at any higher temperature can be calculated from the entropy changes that occur as the substance is warmed to the new temperature. At the very lowest temperatures, this entropy change is calculated by integrating C_P/T, using Debye's theoretical relationship, $C_P=AT^3$; A is obtained from the value of C_P at the lowest temperature for which an experimental value of C_P is available. In temperature ranges where experimental heat capacity data are available, the entropy change is obtained by integration using these data.

Phase changes are isothermal and reversible. Where the substance undergoes phase changes, the contribution that the phase change makes to the entropy of the substance is equal to the enthalpy change for the phase change divided by the temperature at which it occurs.

At any given temperature, the entropy value that is obtained in this way is called the substance's ***absolute entropy*** or its ***third-law entropy***. When the entropy value is calculated for one mole of the substance in its standard state, the resulting absolute entropy is called the ***standard entropy***. The standard entropy is usually given the symbol S^o. It is usually included in compilations of thermodynamic data for chemical substances.

We write $S^o_A\left(T\right)$ to indicate the absolute entropy of substance A in its standard state at temperature T. $S^o_A\left(T\right)$ is the entropy of the substance in its standard state at absolute zero plus the entropy increase that occurs as the substance changes reversibly to its standard state at T. So long as substance A forms a perfect crystal at absolute zero, $S^o_A\left(T\right)$ is the difference between its molar entropy at T and its molar entropy at absolute zero—as calculated from heat capacity and phase-change enthalpy data.

If substance A does not form a perfect crystal at absolute zero, the true value of $S^o_A\left(T\right)$ exceeds the calculated value. The excess is the molar entropy of the imperfect crystal at absolute zero. We observe the discrepancy when measured values, at T, of entropies of reactions that involve A fail to agree with those calculated using the incorrect value of $S^o_A\left(T\right)$.

In Section 11.2 we note that many tables of thermochemical properties present "absolute enthalpy" data for chemical substances. An absolute enthalpy is the difference between the enthalpies of a substance at two different temperatures, but the reference temperature is not absolute zero. In Section 6.4 and Section 6.5, we introduce enthalpy standard states and the standard enthalpy of formation of substance A at temperature T, which we designate as $\Delta_fH^o_A\left(T\right)$. We define the standard enthalpy of formation of any element at any temperature to be zero. In Section 8.6, we find that the enthalpy difference between reactants in their standard states and products in their standard states is readily calculated from the standard enthalpies of formation of the participating substances. As illustrated in Figure 8-2, this calculation is successful because it utilizes an isothermal cycle which begins and ends in a common set of elements, all of which are at the same temperature.

We can also define the standard entropy of formation of any substance to be the difference between its standard entropy, $S^o_A\left(T\right)$, and those of its pure constituent elements in their standard states at the same temperature. This definition is embedded in the Lewis and Randall statement of the third law. For example, the standard entropy of formation of water at 400 K is the difference

$$\Delta_fS^o\left(H_2O,\ 400\ \mathrm{K}\right)=\Delta S^o\left(H_2O,\ 400\mathrm{K}\right)$$

$$-\Delta S^o\left(H_2,\ 400\ \mathrm{K}\right)-\frac{1}{2}\Delta S^o\left(O_2,400\mathrm{K}\right)$$

Because of this definition, the standard entropy of formation of an element in its standard state is zero. We can calculate the standard entropy change for any reaction, $\Delta_rS^o\left(T\right)$, either as the difference between the standard entropies of formation (the $\Delta_fS^o\left(T\right)$ values) of the reactants and products or as the difference between their standard entropies (the $S^o_A\left(T\right)$ values). Either calculation is successful because it begins and ends with a common set of elements, all of which are at the same temperature. When we compute $\Delta_rS^o\left(T\right)$ using values of $S^o_A\left(T\right)$ for the reactants and products the reference temperature for the elements is absolute zero. When we compute $\Delta_rS^o\left(T\right)$ using values of $\Delta_fS^o\left(T\right)$ for the reactants and products, the reference temperature is T.

Given $\Delta_f H^o(T)$ and $\Delta_f S^o(T)$, the standard Gibbs free energy of formation is immediately obtained from $\Delta_f G^o(T) = \Delta_f H^o(T) - T\Delta_f S^o(T)$. For any element at any temperature, we have $\Delta_f H^o = 0$ and $\Delta_f S^o = 0$; it follows that the standard Gibbs free energy of formation of an element in its standard state is zero. Tables of thermodynamic data usually give values for$\Delta_f H^o$, $\Delta_f G^o$, and S^o. (A set of standard entropies contains the same information as the corresponding set of entropies of formation. Entropies of formation are seldom tabulated. If $\Delta_f S^o$ is needed, it can be calculated either from $\Delta_f H^o$ and $\Delta_f G^o$ or from the absolute entropies of the substance and the elements from which it is formed.)

3.12: Evaluating Entropy Changes Using Thermochemical Cycles

As for the standard enthalpy of reaction, we can obtain the standard entropy of reaction at a new temperature by evaluating entropy changes around a suitable thermochemical cycle. To do so, we need the standard entropy change at one temperature. We also need heat capacity data for all of the reactants and products. For the reaction

$$a\,A+b\,B\rightarrow c\,C+d\,D$$

we can evaluate the entropy change at a second temperature by summing the individual contributions to the change in entropy around the cycle in Figure 5. For this cycle, we have

$$\Delta_rS^o\left(T_2\right)=\Delta_rS^o\left(T_1\right)+c\int^{T_2}_{T_1}{\frac{C_P\left(C\right)}{T}}dT+d\int^{T_2}_{T_1}{\frac{C_P\left(D\right)}{T}}dT-a\int^{T_2}_{T_1}{\frac{C_P\left(A\right)}{T}}dT-b\int^{T_2}_{T_1}{\frac{C_P\left(B\right)}{T}}dT$$

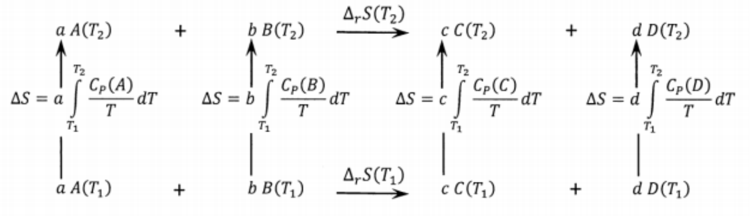

Figure 5. Cycle relating the entropy changes for a reaction at two temperatures.

CHAPTER OVERVIEW

4: State Functions in Thermodynamics

4.1: Free Energy Functions

In the previous chapter, we saw that for a spontaneous process, $\Delta S_{universe} > 0$. While this is a useful criterion for determining whether or not a process is spontaneous, it is rather cumbersome, as it requires one to calculate not only the entropy change for the system, but also that of the surroundings. It would be much more convenient if there was a single criterion that would do the job and focus only on the system. As it turns out, there is.

Since we know that

$$\Delta S_{univ} \geq 0$$

for any natural process, and

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

all we need to do is to find an expression for ΔS_{sys} that can be determined by the changes in the system itself. Fortunately, we have already done that! Recalling that at constant temperature

$$\Delta S = -\frac{q_{rev}}{T}$$

and at constant pressure

$$\Delta H = q_p$$

it follows that at constant temperature and pressure

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$

Substitution into the above equations yields an expression for the criterion of spontaneity that depends only on variables describing the changes in the system!

$$\Delta S_{univ} \geq \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

so

$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0$$

Multiplying both sides by $-T$ yields

$$\Delta H - T\Delta S \leq 0 \tag{4.1.1}$$

A similar derivation for constant volume processes results in the expression (at constant volume and temperature)

$$\Delta U - T\Delta S \leq 0 \tag{4.1.2}$$

> Equation 4.1.1 is of great use to chemists, as most of chemistry occurs at constant pressure. For geologists, however, who are interested in processes that occur at very high pressures (say, under the weight of an entire mountain) and expansion is not a possibility, the constant volume expression of Equation 4.1.1 may be of greater interest.

All of the above arguments can be made for systems in which the temperature is not constant by considering infinitesimal changes. The resulting expressions are

$$dH - TdS \leq 0 \tag{4.1.3}$$

and

$$dU - TdS \leq 0 \tag{4.1.4}$$

The Gibbs and Helmholtz Functions

Equation 4.1.3 suggests a very convenient thermodynamic function to help keep track of both the effects of entropy and enthalpy changes. This function, the **Gibbs function** (or **Gibbs Free Energy**) is defined by

$$G \equiv H - TS$$

A change in the Gibbs function can be expressed

$$\Delta G = \Delta H - \Delta(TS)$$

Or at constant temperature

$$\Delta G = \Delta H - T\Delta S$$

And the criterion for a process to be spontaneous is the DG < 0. As such, it should be clear spontaneity is not merely a function the enthalpy change (although exothermic processes tend to be spontaneous) but also a function of the entropy change, weighted by the temperature. Going back to an earlier example,

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

with $\Delta H < 0$.

and

$$NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq)$$

with $\Delta H > 0$.

It is easy to see why both processes are spontaneous. In the first case, the process is exothermic (favorable) and proceeds with an increase in entropy (also favorable) due to the formation of fragments in the liquid phase (more chaotic) from a very ordered solid (more ordered). The second reaction is endothermic (unfavorable) but proceeds with an increase in entropy (favorable). So, so long as the temperature is high enough, the entropy term will overwhelm the enthalpy term and cause the process to be spontaneous. The conditions for spontaneous processes at constant temperature and pressure can be summarized in Table 6.1.1.

Table 6.1.1: Spontaneity Conditions for a Process under Constant Temperature and Pressure

ΔH	ΔS	**Spontaneous**
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T
< 0	< 0	At low T

Similarly to the Gibbs function, the **Helmholtz function** is defined by

$$A \equiv U - TS$$

and provides another important criterion for spontaneous processes at constant value and temperature. *At constant temperature*, the Helmholtz function can be expressed by

$$\Delta A \equiv \Delta U - T\Delta S$$

Based on similar arguments used for the Gibbs function, the Helmholtz function also can be used to predict which processes will be spontaneous at constant volume and temperature according to Table 6.1.2.

Table 6.1.2: Spontaneity Conditions for a Process under Constant Temperature and Volume

ΔU	ΔS	**Spontaneous?**
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T

ΔU	ΔS	Spontaneous?
< 0	< 0	At low T

Calculating ΔG for Reactions

Much like in the case of enthalpy (and unlike entropy), free energy functions do not have an unambiguous zero to the energy scale. So, just like in the case of enthalpies of formation, by convention, the standard free energy of formation (ΔG_f^o) for elements in their standard states is defined as zero. This allows for two important things to happen. First, ΔG_f^o can be measured and tabulated for any substance (in principle, at least.) ΔG_f^o is determined to be ΔG_{rxn}^o for the reaction that forms one mole of a compound from elements in their standard states (similarly to how ΔH_f^o is defined.) Secondly, tabulated (ΔG_f^o) can be used to calculate standard reaction free energies (ΔG_{rxn}^o) in much the same way as ΔH_f^o is used for reaction enthalpies.

✓ Example 4.1.1:

Given the following data at 298 K, calculate ΔG^o at 298 K for the following reaction:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Substance	ΔG_f^o (kJ/mol)
C_2H_4(g)	68.4
C_2H_6(g)	-32.0

Solution

The ΔG_f^o values can be used to calculate ΔG^o for the reaction in exactly the same method as ΔH_f^o can be used to calculate a reaction enthalpy.

$$\Delta G^o = (1\,mol)(-32.0\,kJ/mol) - (1\,mol)(68.4\,kJ/mol)$$

$$\Delta G^o = 100.4\,kJ$$

Note: $H_2(g)$ is not included in the calculation since ΔG_f^o for $H_2(g)$ is 0 since it is an element in its standard state.

4.2: ΔA, ΔG, and Maximum Work

The functions A and G are oftentimes referred to as **free energy** functions. The reason for this is that they are a measure of the maximum work (in the case of ΔA) or non p-V work (in the case of ΔG) that is available from a process. To show this, consider the total differentials.

First, consider the differential of A.

$$dA = dU - TdS - SdT$$

Substituting the combined first and second laws for dU, but expressing the work term as dw, yields

$$dA = TdS - dw - TdS - SdT$$

And cancelling the TdS terms gives

$$dA = dw - SdT$$

or at constant temperature ($dT = 0$)

$$dA = dw$$

Since the only assumption made here was that the change is reversible (allowing for the substitution of TdS for dq), and dw for a reversible change is the maximum amount of work, it follows that dA gives the maximum work that can be produced from a process at constant temperature.

Similarly, a simple expression can be derived for dG. Starting from the total differential of G.

$$dG = dU + pdV - pdV + Vdp - TdS - SdT$$

Using an expression for $dU = dq + dw$, where $dq = TdS$ and dw is split into two terms, one (dw_{pV}) describing the work of expansion and the other (dw_e) describing any other type of work (electrical, stretching, etc.)

$$dU - TdS + dW_{pV} + dW_e$$

dG can be expressed as

$$dG = T\cancel{dS} - p\cancel{dV} + dw_e + p\cancel{dV} + Vdp - T\cancel{dS} - SdT$$

Cancelling the TdS and pdV terms leaves

$$dG = +dw_e + Vdp - SdT$$

So at constant temperature ($dT = 0$) and pressure ($dp = 0$),

$$dG = dw_e$$

This implies that dG gives the maximum amount of non p-V work that can be extracted from a process.

This concept of dA and dG giving the maximum work (under the specified conditions) is where the term “free energy” comes from, as it is the energy that is *free* to do work in the surroundings. If a system is to be optimized to do work in the soundings (for example a steam engine that may do work by moving a locomotive) the functions A and G will be important to understand. It will, therefore, be useful to understand how these functions change with changing conditions, such as volume, temperature, and pressure.

Contributors

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4.3: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

The Helmholtz energy A is developed for isochoric changes and as we have often said before it is much easier to deal with isobaric ones where $P =$ constant. We can therefore repeat the above treatment for the enthalpy and introduce another state function the Gibbs energy

$$\begin{aligned} G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

If we take both T and P constant we get

$$dU - TdS + PdV \leq 0$$

$$dG \leq 0$$

G either decreases (spontaneously) or is constant (at equilibrium). Calculating the state function between two end points we get:

$$\Delta G = \Delta H - T\Delta S \leq 0 (T, P \text{ constant})$$

This quantity is key to the question of spontaneity under the conditions we usually work under. If for a process ΔG is positive it does not occur spontaneous and can only be made to occur if it is 'pumped', i.e. coupled with a process that has a negative ΔG. The latter is spontaneous.

> If $\Delta G = 0$ then the system is as ***equilibrium***.

4.3.1: Direction of the spontaneous change

Because the ΔS term contains the temperature T as coefficient the spontaneous direction of a process, e.g. a chemical reaction can **change** with temperature depending on the values of the enthalpy and the entropy change ΔH and ΔS. This is true for the melting process, e.g. for water below 0^oC we get water=>ice, above this temperature ice melts to water, but it also goes for chemical reactions.

✓ Example

Consider

$$\mathrm{NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)}$$

$\Delta_r H$ at 298K / 1 bar is -176.2 kJ. The change in entropy is -0.285 kJ/K so that at 298K ΔG is -91.21 kJ. Clearly this is a reaction that will proceed to the depletion of whatever is the limiting reagent on the left.

However at 618 K this is a different story. Above this temperature ΔG is positive! (assuming enthalpy and entropy have remained the same, which is almost but not completely true) The reaction will not proceed. Instead the *reverse* reaction would proceed spontaneously. The salt on the right would decompose in the two gases -base and acid- on the left.

4.3.2: Meaning of the ΔG term

As we have seen, ΔA can be related to the maximal amount of work that a system can perform at constant V and T. We can hold an analogous argument for ΔG except that V is not constant so that we have to consider volume work (zero at constant volume) .

$$dG = d(U + PV - TS) = dU - TdS - SdT - PdV + VdP$$

As $dU = TdS + \delta w_{rev}$

$$dG = \delta w_{rev} - SdT + VdP + PdV$$

As the later term is $-\delta w_{volume}$

$$dG = \delta w_{rev} - SdT + VdP - \delta w_{volume}$$

At constant T and P the two middle terms drop out

$$dG = \delta w_{rev} - \delta w_{volume} = \delta w_{otherusefulwork}$$

Note

ΔG stands for the (maximal) reversible, isobaric isothermal non-PV work that a certain spontaneous change can perform. The volume work may not be zero, but is corrected for.

4.3.3: Natural variables of G

Because $G \equiv H - TS$, we can write

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT = VdP - SdT \end{aligned}$$

The natural variables of G are pressure P and temperature T. This is what makes this function the most useful of the four U, H, A, and G: these are the natural variables of most of your laboratory experiments!

4.3.4: Summary

We now have developed the basic set of concepts and functions that together form the framework of thermodynamics. Let's summarize four very basic state functions:

state function	natural variables
$dU = -PdV + TdS$	$U(V,S)$
$dH = +VdP + TdS$	$H(P,S)$
$dA = -PdV - SdT$	$A(V,T)$
$dG = +VdP - SdT$	$G(P,T)$

Note:

1. The replacement of δq by TdS was based on *reversible* heat. This means that in the irreversible case the expressions for dU and dH become inequalities
2. We only include *volume* work in the above expressions. If other work (elastic, electrical e.g.) is involved extra terms need to be added: $dU = TdS - PdV + xdX$ etc.

We are now ready to begin applying thermodynamics to a number of very diverse situations, but we will first develop some useful partial differential machinery.

4.4: The Maxwell Relations

Modeling the dependence of the Gibbs and Helmholtz functions behave with varying temperature, pressure, and volume is fundamentally useful. But in order to do that, a little bit more development is necessary. To see the power and utility of these functions, it is useful to combine the First and Second Laws into a single mathematical statement. In order to do that, one notes that since

$$dS = \frac{dq}{T}$$

for a reversible change, it follows that

$$dq = TdS$$

And since

$$dw = TdS - pdV$$

for a reversible expansion in which only p-V works is done, it also follows that (since $dU = dq + dw$):

$$dU = TdS - pdV$$

This is an extraordinarily powerful result. This differential for dU can be used to simplify the differentials for H, A, and G. But even more useful are the constraints it places on the variables T, S, p, and V due to the mathematics of exact differentials!

4.4.1: Maxwell Relations

The above result suggests that the natural variables of internal energy are S and V (or the function can be considered as $U(S,V)$). So the total differential (dU) can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Also, by inspection (comparing the two expressions for dU) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{4.4.1}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{4.4.2}$$

But the value doesn't stop there! Since dU is an exact differential, the Euler relation must hold that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

By substituting Equations 4.4.1 and 4.4.2, we see that

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

or

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

This is an example of a **Maxwell Relation**. These are very powerful relationship that allows one to substitute partial derivatives when one is more convenient (perhaps it can be expressed entirely in terms of α and/or κ_T for example.)

A similar result can be derived based on the definition of H.

$$H \equiv U + pV$$

Differentiating (and using the chain rule on $d(pV)$) yields

$$dH = dU + pdV + Vdp$$

Making the substitution using the combined first and second laws ($dU = TdS - pdV$) for a reversible change involving on expansion (p-V) work

$$dH = TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$

This expression can be simplified by canceling the pdV terms.

$$dH = TdS + Vdp \tag{4.4.3}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{4.4.4}$$

Comparing Equations 4.4.3 and 4.4.4 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{4.4.5}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{4.4.6}$$

It is worth noting at this point that both (Equation 4.4.1)

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and (Equation 4.4.5)

$$\left(\frac{\partial H}{\partial S}\right)_p$$

are equation to T. So they are equation to each other

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

Morevoer, the Euler Relation must also hold

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p$$

so

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

This is the Maxwell relation on H. Maxwell relations can also be developed based on A and G. The results of those derivations are summarized in Table 6.2.1..

Table 6.2.1: Maxwell Relations

Function	Differential	Natural Variables	Maxwell Relation
U	$dU = TdS - pdV$	S, V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	$dH = TdS + Vdp$	S, p	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

Function	Differential	Natural Variables	Maxwell Relation
A	$dA = -pdV - SdT$	V, T	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	$dG = Vdp - SdT$	p, T	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of p, T, and V.

✓ Example 4.4.1

Show that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

Solution

Start with the combined first and second laws:

$$dU = TdS - pdV$$

Divide both sides by dV and constraint to constant T:

$$\left.\frac{dU}{dV}\right|_T = \left.\frac{TdS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$\left.\frac{TdS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left.\frac{dV}{dV}\right|_T = 1$$

The result is

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

Now, employ the Maxwell relation on A (Table 6.2.1)

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

to get

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

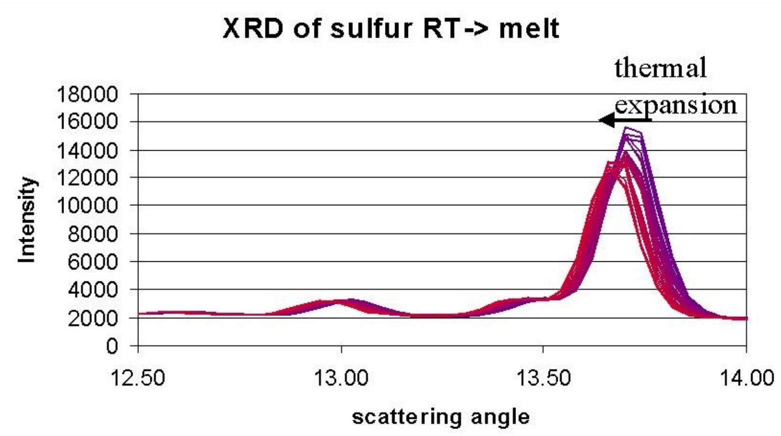
and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

It is apparent that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

> *Note*: How cool is that? This result was given without proof in Chapter 4, but can now be proven analytically using the Maxwell Relations!



4.5: Volume Dependence of Helmholtz Energy

If one needs to know how the Helmholtz function changes with changing volume at constant temperature, the following expression can be used:

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV \tag{4.5.1}$$

But how does one derive an expression for the partial derivative in Equation 4.5.1? This is a fairly straight forward process that begins with the definition of A:

$$A = U - TS$$

Differentiating (and using the chain rule to evaluate $d(TS)$ yields

$$dA = dU - TdS - SdT \tag{4.5.2}$$

Now, it is convenient to use the combined first and second laws

$$dU = TdS - pdV \tag{4.5.3}$$

which assumes:

1. a reversible change and
2. only pV work is being done.

Substituting Equation 4.5.3 into Equation 4.5.2 yields

$$dA = \cancel{TdS} - pdV - \cancel{TdS} - SdT \tag{4.5.4}$$

Canceling the TdS terms gives the important result

$$dA = -pdV - SdT \tag{4.5.5}$$

The natural variables of A are therefore V and T! So the total differential of A is conveniently expressed as

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \tag{4.5.6}$$

and by simple comparison of Equations 4.5.5 and 4.5.6, it is clear that

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

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

And so, one can evaluate Equation 4.5.1 as

$$\Delta A = -\int_{V_1}^{V_2} p\, dV$$

If the pressure is independent of the temperature, it can be pulled out of the integral.

$$\Delta A = -p\int_{V_1}^{V_2} dV = -p(V_2 - V_1)$$

Otherwise, the temperature dependence of the pressure must be included.

$$\Delta A = -\int_{V_1}^{V_2} p(V)\, dV$$

Fortunately, this is easy if the substance is an ideal gas (or if some other equation of state can be used, such as the van der Waals equation.)

✓ Example $4.5.1$: Ideal Gas Expansion

Calculate ΔA for the isothermal expansion of 1.00 mol of an ideal gas from 10.0 L to 25.0 L at 298 K.

Solution

For an ideal gas,

$$p = \frac{nRT}{V}$$

So

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

becomes

$$\left(\frac{\partial A}{\partial V}\right)_T = -\frac{nRT}{V}$$

And so (Equation $4.5.1$)

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV$$

becomes

$$\Delta A = -nRT \int_{V_1}^{V_2} \frac{dV}{V} dT$$

or

$$\Delta A = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Substituting the values from the problem

$$\Delta A = -(1.00\, mol)(8.314\, J/(mol\, K))(298\, K) \ln\left(\frac{25.0\, L}{10.0\, L}\right)$$

But further, it is easy to show that the Maxwell relation that arises from the simplified expression for the total differential of A is

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

This particular Maxwell relation is exceedingly useful since one of the terms depends only on p, V, and T. As such it can be expressed in terms of our old friends, α and κ_T!

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

4.6: Pressure Dependence of Gibbs Energy

The pressure and temperature dependence of G is also easy to describe. The best starting place is the definition of G.

$$G = U + pV - TS \tag{4.6.1}$$

Taking the total differential of G yields

$$dG = dU + pdV - pdV + Vdp - TdS - SdT$$

The differential can be simplified by substituting the combined first and second law statement for dU (consider a reversible process and pV work only).

$$dG = \cancel{TdS} \cancel{-pdV} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

Canceling the TdS and pdV terms leaves

$$dG = V\,dp - S\,dT \tag{4.6.2}$$

This suggests that the natural variables of G are p and T. So the total differential dG can also be expressed

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{4.6.3}$$

And by inspection of Equations 4.6.2 and 4.6.3, it is clear that

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

and

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

It is also clear that the Maxwell relation on G is given by

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

which is an extraordinarily useful relationship, since one of the terms is expressible entirely in terms of measurable quantities!

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

The pressure dependence of G is given by the pressure derivative at constant temperature

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{4.6.4}$$

which is simply the molar volume. For a fairly incompressible substance (such as a liquid or a solid) the molar volume will be essentially constant over a modest pressure range.

✓ Example 4.6.1: Gold under Pressure

The density of gold is 19.32 g/cm^3. Calculate ΔG for a 1.00 g sample of gold when the pressure on it is increased from 1.00 atm to 2.00 atm.

Solution

The change in the Gibbs function due to an isothermal change in pressure can be expressed as

$$\Delta G = \int_{p_1}^{p_2} \left(\frac{\partial G}{\partial p}\right)_T dp$$

And since substituting Equation 4.6.4, results in

$$\Delta G = \int_{p_1}^{p_2} V dp$$

Assuming that the molar volume is independent or pressure over the stated pressure range, ΔG becomes

$$\Delta G = V(p_2 - p_1)$$

So, the molar change in the Gibbs function can be calculated by substituting the relevant values.

$$\Delta G = \left(\frac{197.0\, g}{mol} \times \frac{1}{19.32\, g} \times \frac{1\, L}{1000\, cm^3}\right)(2.00\, atm - 1.00\, atm)\underbrace{\left(\frac{8.315\, J}{0.08206\, atm\, L}\right)}_{\text{conversion unit}} \tag{4.6.5}$$

$$= 1.033\, J \tag{4.6.6}$$

Contributors

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4.7: Temperature Dependence of A and G

In differential form, the free energy functions can be expressed as

$$dA = -pdV - SdT$$

and

$$dG = -V\,dp - SdT$$

So by inspection, it is easy to see that

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

and

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

And so, it should be fairly straightforward to determine how each changes with changing temperature:

$$\Delta A = -\int_{T_1}^{T_2} \left(\frac{\partial A}{\partial T}\right)_V dT = -\int_{T_1}^{T_2} S\,dT$$

and

$$\Delta G = -\int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_p dT = -\int_{T_1}^{T_2} S\,dT$$

But the temperature dependence of the entropy needed to be known in order to evaluate the integral. A convenient work-around can be obtained starting from the definitions of the free energy functions.

$$A = U - TS$$

and

$$G = H - TS$$

Dividing by T yields

$$\frac{A}{T} = \frac{U}{T} - S$$

and

$$\frac{G}{T} = \frac{H}{T} - S$$

Now differentiating each expression with respect to T at constant V or p respectively yields

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

and

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p = -\frac{H}{T^2}$$

Or differentiating with respect to $1/T$ provides a simpler form that is mathematically equivalent:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_V = U$$

and

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = H$$

Focusing on the second expression (since all of the arguments apply to the first as well), we see a system that can be integrated. Multiplying both sides by $d(1/T)$ yields:

$$d\left(\frac{G}{T}\right) = Hd\left(\frac{1}{T}\right)$$

Or for finite changes ΔG and ΔH:

$$d\left(\frac{\Delta G}{T}\right) = \Delta Hd\left(\frac{1}{T}\right)$$

and integration, assuming the *enthalpy change is constant over the temperature* interval yields

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \Delta H\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.7.1}$$

Equation ??? is the **Gibbs-Helmholtz equation** and can be used to determine how ΔG changes with changing temperature. The equivalent equation for the Helmholtz function is

$$\frac{\Delta A_{T_2}}{T_2} - \frac{\Delta A_{T_1}}{T_1} = \Delta U\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.7.2}$$

✓ Example 4.7.1:

Given the following data at 298 K, calculate ΔG at 500 K for the following reaction:

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

Compound	**ΔG_f^o (kJ/mol)**	**ΔH_f^o (kJ.mol)**
CH_4(g)	-50.5	-74.6
CO_2(g)	-394.4	-393.5
H_2O(g)	-228.6	-241.8

Solution

ΔH and $\Delta G_{298\ K}$ and can be calculated fairly easily. It will be assumed that ΔH is constant over the temperature range of 298 K – 500 K.

$$\Delta H = (1\ mol)(-393.5\ kJ/mol) + (2\ mol)(-241.8\ kJ/mol) – (1\ mol)(-74.5\ kJ/mol) = -820.6\ kJ$$

$$\Delta G_{298} = (1\ mol)(-394.4\ kJ/mol) + (2\ mol)(-228,6\ kJ/mol) – (1\ mol)(-50.5\ kJ/mol) = -801.1\ kJ$$

So using Equation 4.7.1 with the data just calculated gives

$$\frac{\Delta G_{500\ K}}{500\ K} - \frac{-801.1\ kJ}{298\ K} = (-820.6\ kJ)\left(\frac{1}{500\ K} - \frac{1}{298\ K}\right)$$

$$\Delta G_{500\ K} = -787.9\ kJ$$

Note: ΔG became a little bit less negative at the higher temperature, which is to be expected for a reaction which is exothermic. An increase in temperature should tend to make the reaction less favorable to the formation of products, which is exactly what is seen in this case!

4.8: The Enthalpy of an Ideal Gas is Independent of Pressure

How does pressure affect enthalpy H? As we showed above we have the following relations of first and second order for G

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = -V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

We also know that by definition:

$$G = H - TS \tag{4.8.1}$$

Consider an isothermal change in pressure, so taking the partial derivative of each side of Equation 4.8.1, we get:

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{4.8.2}$$

For an ideal gas

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

so Equation 4.8.2 becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{nR}{P}\right) = 0$$

As we can see for an ideal gas, there is no dependence of H on P.

- **22.4: The Enthalpy of an Ideal Gas is Independent of Pressure** is licensed CC BY-NC-SA 4.0.

4.9: When Two Variables Change at Once

So far, we have derived a number of expressions and developed methods for evaluating how thermodynamic variables change as one variable changes while holding the rest constant. But real systems are seldom this accommodating. For example, a piece of metal (such as a railroad rail) left in the sun will undergo both an increase in temperature and an expansion due to the absorption of energy from sunlight. So both T and V are changing at the same time! If the change in a thermodynamic variable (such as G) is needed, contributions from both changes are required to be taken into account. We've already seen how to express this in terms of a total differential.

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{4.9.1}$$

Fortunately, G (like the other thermodynamic functions U, H, S, and A) is kind enough to be a state variable. This means that we can consider the changes independently and then simply add the results. Another way to think of this is that the system may follow either of two pathways to get from the initial conditions to the final conditions:

- *Pathway I:*
  1. An isothermal expansion from V_1 to V_2 at T_1 followed by
  2. An isochoric temperature increase from T_1 to T_2 at V_2
- *Pathway 2:*
  1. An isochoric temperature increase from T_1 to T_2 at V_1 followed by
  2. And isothermal expansion from V_1 to V_2 at T_2

And since G has the good sense to be a state variable, the pathway connecting the initial and final states is unimportant. We are free to choose any path that is convenient to calculate the change.

✓ Example 4.9.1: Non-Isothermal Gas Expansion

Calculate the entropy change for 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) expanding from 10.0 L at 273 K to 22.0 L at 297 K.

Solution

If one considers entropy to be a function of temperature and volume, one can write the total differential of entropy as

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

and thus

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

The first term is the contribution due to an *isochoric temperature* change:

$$\begin{align} \Delta S_{T_1 \rightarrow T_2} &= \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT \tag{4.9.2} \\ &= \int_{T_1}^{T_2} \frac{nC_V}{T} dT \tag{4.9.3} \\ &= nC_V \ln\left(\frac{T_2}{T_1}\right) \tag{4.9.4} \\ &= (1.00\, mol)\left(\frac{3}{2} \cdot 8.314 \frac{J}{mol\ K}\right) \ln\left(\frac{297\ K}{273\ K}\right) \tag{4.9.5} \\ &= 13.57\ J/K \tag{4.9.6} \end{align}$$

The second term is the contribution due to an isothermal expansion:

$$\Delta S_{V_1\to V_2} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV \tag{4.9.7}$$

From the Maxwell relation on A

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

So Equation 4.9.7 becomes

$$\Delta S_{V_1\to V_2} = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV \tag{4.9.8}$$

$$= \int_{V_1}^{V_2} \left(\frac{nR}{V}\right) dV \tag{4.9.9}$$

$$= nR\ln\left(\frac{V_2}{V_1}\right) \tag{4.9.10}$$

$$= (1.00\, mol)\left(8.314\frac{J}{mol\, K}\right)\ln\left(\frac{22.0\, L}{10.0\, L}\right) \tag{4.9.11}$$

$$= 6.56\, J/K \tag{4.9.12}$$

And the total entropy change is

$$\Delta S_{tot} = \Delta S_{V_1\to V_2} + \Delta S_{V_1\to V_2} \tag{4.9.13}$$

$$= 13.57\, J/K + 6.56\, J/K \tag{4.9.14}$$

$$= 20.13\, J/K \tag{4.9.15}$$

Deriving an expression for a partial derivative (Type III)

Thermodynamics involves many variables. But for a single component sample of matter, only two state variables are needed to describe the system and fix all of the thermodynamic properties of the system. As such, it is conceivable that two functions can be specified as functions of the same two variables. In general terms: $z(x, y)$ and $w(x, y)$.

So an important question that can be answered is, “What happens to z if w is held constant, but x is changed?” To explore this, consider the total differential of z:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{4.9.16}$$

but z can also be considered a function of x and $w(x, y)$. This implies that the total differential can also be written as

$$dz = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dy \tag{4.9.17}$$

and these two total differentials must be equal to one another!

$$= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dw$$

If we constrain the system to a change in which w remains constant, the last term will vanish since $dw = 0$.

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = \left(\frac{\partial z}{\partial x}\right)_w dx \tag{4.9.18}$$

but also, since w is a function x and y, the total differential for w can be written

$$dw = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy$$

And it too must be zero for a process in which w is held constant.

$$0=\left(\frac{\partial w}{\partial x}\right)_y dx+\left(\frac{\partial w}{\partial y}\right)_x dy$$

From this expression, it can be seen that

$$dy=-\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial y}{\partial w}\right)_x dx$$

Substituting this into the Equation 4.9.18, yields

$$\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x\left[-\left(\frac{\partial w}{\partial x}\right)_y\left(\frac{\partial y}{\partial w}\right)_x dx\right]=\left(\frac{\partial z}{\partial x}\right)_w dx \tag{4.9.19}$$

which simplifies to

$$\left(\frac{\partial z}{\partial x}\right)_y dx-\left(\frac{\partial z}{\partial w}\right)_x\left(\frac{\partial w}{\partial x}\right)_y dx=\left(\frac{\partial z}{\partial x}\right)_w dx$$

So for $dx\neq 0$, implies that

$$\left(\frac{\partial z}{\partial x}\right)_y-\left(\frac{\partial z}{\partial w}\right)_x\left(\frac{\partial w}{\partial x}\right)_y=\left(\frac{\partial z}{\partial x}\right)_w$$

or

$$\left(\frac{\partial z}{\partial x}\right)_y=\left(\frac{\partial z}{\partial x}\right)_w+\left(\frac{\partial z}{\partial w}\right)_x\left(\frac{\partial w}{\partial x}\right)_y \tag{4.9.20}$$

As with partial derivative transformation types I and II, this result can be achieved in a formal, albeit less mathematically rigorous method.

Consider $z(x,w)$. This allows us to write the total differential for z:

$$dz=\left(\frac{\partial z}{\partial x}\right)_w dx+\left(\frac{\partial z}{\partial w}\right)_x dw$$

Now, divide by dx and constrain to constant y.

$$\left.\frac{dz}{dx}\right|_y=\left(\frac{\partial z}{\partial x}\right)_w\left.\frac{dx}{dx}\right|_y+\left(\frac{\partial z}{\partial w}\right)_x\left.\frac{dw}{dx}\right|_y$$

noting that $dx/dx=1$ and converting the other ratios to partial derivatives yields

$$\left(\frac{\partial z}{\partial x}\right)_y=\left(\frac{\partial z}{\partial x}\right)_w+\left(\frac{\partial z}{\partial w}\right)_x\left(\frac{\partial w}{\partial x}\right)_y \tag{4.9.21}$$

which agrees with the previous result (Equation 4.9.20)! Again, the method is not mathematically rigorous, but it works so long as w, x, y, and z are **state functions** and the total differentials dw, dx, dy, and dz are **exact**.

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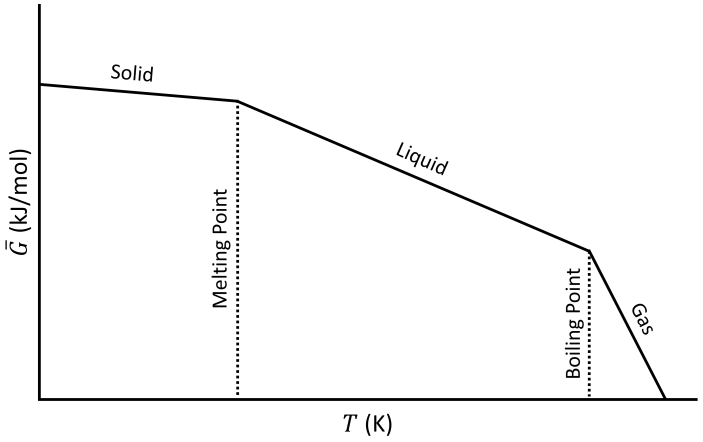
CHAPTER OVERVIEW

5: Single Component Phase Equilibrium

5.1: Gibbs Energies and Phase Diagrams

5.1.1: First Order Transitions

The following plot shows the Gibbs energy as a function of temperature, including phase changes from solid to liquid (melting) and liquid to gas (boiling).



Gibbs energy ($\bar{G}$) as a function of temperature (T).

Although the G curve is continuous, its first order derivatives ($-S$) is discontinuous at the phase changes. This is why this transition it called a *first order transition*. We could say that:

- G is continuous but has a kink
- The first order derivatives (H,S,..) are discontinuous (have a jump)
- The second order derivatives (C_P, ..) have a singularity (go to ∞)

5.1.2: Second Order Transitions

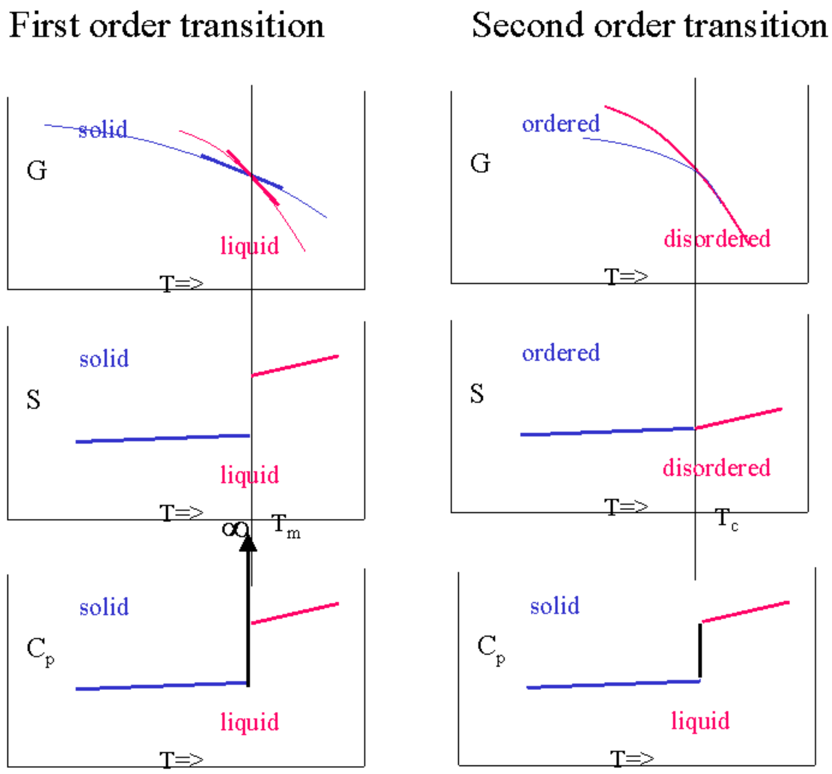
More subtle transitions where G is continuous, H and S are also continuous but have a kink and the discontinuity is only found in the second order derivatives (such as C_P) also exist. They are called *second order transitions*. In such a case:

- G is continuous and has no kink
- The first order derivatives (H,S,..) are continuous (but have a kink)
- The second order derivatives (C_P, ..) are discontinuous (have a jump)

Table 23.2.1: Properties of Phase Transitions

Transition Order	**Function**	**1st Order**	**2nd Order**
0	G,A	kink	smooth
1	H,S,V,..	jump	kink
2	CP,CV,α,κ	sing. ∞	jump

This classification goes back to Ehrenfest. Obviously it based on the question: what order derivative is the first to go discontinuous? Of course we could extend this principle and define *third order transitions* but there are reasons to be doubtful that such things exist. Another problem is that it is assumed that the order must be integer: 1,2, etc. Is it possible to have a transition of intermediate non-integer order, say 1.3? Although derivatives of fractional order are beyond the scope of the chemistry curriculum the mathematics does exist (Liouville).



Schematic comparison of G, S and C_P for 1st and 2nd order 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.

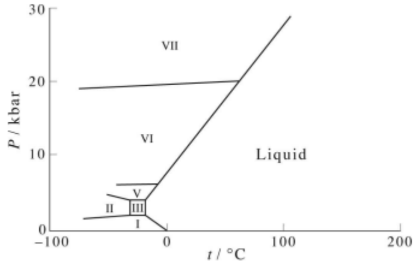


Figure 13.4: Some of the ice polymorphs.

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.

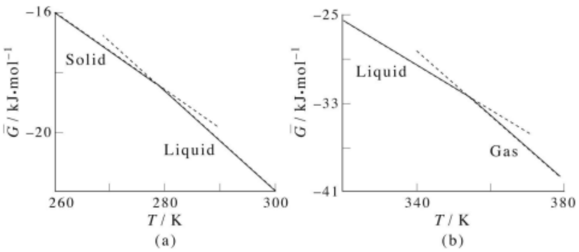


Figure 13.5: Behavior of the Gibbs free energy across the solid-liquid phase (left) and liquid-gas (right) transitions for benzene.

Now, recall that

$$S = -\frac{\partial G}{\partial T} \tag{5.1.1}$$

Consider the slopes in the solid and liquid parts of the graph:

$$\frac{\partial G^{(\mathrm{solid})}}{\partial T} = -S^{(\mathrm{solid})}, \qquad \frac{\partial G^{(\mathrm{liquid})}}{\partial T} = -S^{(\mathrm{liquid})} \tag{5.1.2}$$

However, since

$$\frac{\partial G^{(\mathrm{liquid})}}{\partial T} < \frac{\partial G^{(\mathrm{solid})}}{\partial T} \tag{5.1.3}$$

(*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 $-S^{(\mathrm{liquid})} < -S^{(\mathrm{solid})}$ or $S^{(\mathrm{liquid})} > S^{(\mathrm{solid})}$. 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:

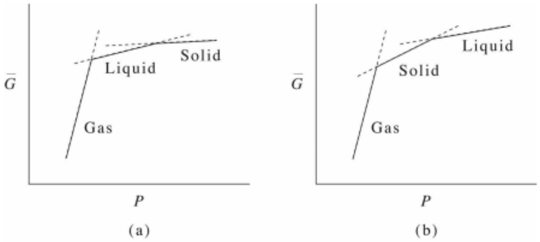


Figure 13.6: Dependence of the Gibbs free energy as a function of pressure for benzene (left) and water (right). For benzene, the temperature is above the triple point, whereas for water, it is set below triple point.

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

$$\bar{V} = \frac{\partial \bar{G}}{\partial P} \tag{5.1.4}$$

From the graph, we see that the slopes obey

$$\bar{V}^{(\mathrm{gas})} \gg \bar{V}^{(\mathrm{liquid})} > \bar{V}^{(\mathrm{solid})} \tag{5.1.5}$$

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

$$\bar{V}^{(\mathrm{gas})} \gg \bar{V}^{(\mathrm{solid})} > \bar{V}^{(\mathrm{liquid})} \tag{5.1.6}$$

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.

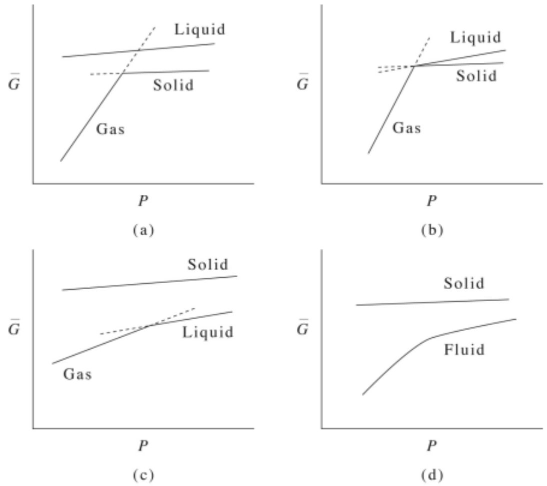


Figure 13.7: Behavior of the Gibbs free energy as a function of P across different phases at different temperatures for benzene. (a): Temperature is less than the triple point; (b): Temperature is equal to the triple point; (c): Temperature is just below the critical temperature; (d): Temperature is greater than the critical temperature.

5.1.3: Conjugate Variables

As discussed before there are many other forms of work possible, such as electrical work, magnetic work or elastic work. These they are commonly incorporated in the formalism of thermodynamics by adding other terms, e.g:

$$dG = -SdT + VdP + \mathcal{E}de + MdH + FdL + \gamma dA$$

1. $\mathcal{E}de$ stands for the electromotoric force $\mathcal{E}$ and de the amount of charge transported against it.
2. MdH stand for magnetization and (change in) magnetic field.
3. F stands for the elastic force of e.g. a rubber band dL for the length it is stretched
4. γ stands for the surface tension (e.g. of a soap bubble), A for its surafce area.

The terms always appear in a pair of what is known as conjugate variables. That is even clearer if we write out the state function rather than its differential form:

$$G = U + PV - TS + \mathcal{E}e + MH + FL + \gamma A + \ldots$$

The PV term can also be generalized -and needs to be so- for a viscous fluid to a stress-strain conjugate pair. It then involves a stress tensor. We will soon encounter another conjugate pair: μdn that deals with changes in composition (n) and the thermodynamic potential μ.

5.2: Chemical Potential and Fugacity

The **chemical potential**, μ, of a pure substance has as one of its definitions (Sec. 5.5)

$$\mu \overset{\text{def}}{=} G_{\text{m}} = \frac{G}{n} \tag{7.8.1}$$
(pure substance)

That is, μ is equal to the molar Gibbs energy of the substance at a given temperature and pressure. (Section 9.2.6 will introduce a more general definition of chemical potential that applies also to a constituent of a mixture.) The chemical potential is an intensive state function.

The total differential of the Gibbs energy of a fixed amount of a pure substance in a single phase, with T and p as independent variables, is $\text{d}G = -S\,\text{d}T + V\,\text{d}p$ (Eq. 5.4.4). Dividing both sides of this equation by n gives the total differential of the chemical potential with these same independent variables:

$$\text{d}\mu = -S_{\text{m}}\,\text{d}T + V_{\text{m}}\,\text{d}p \tag{7.8.2}$$
(pure substance, P=1)

(Since all quantities in this equation are intensive, it is not necessary to specify a closed system; the amount of the substance in the system is irrelevant.)

We identify the coefficients of the terms on the right side of Eq. 7.8.2 as the partial derivatives

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -S_{\text{m}} \tag{7.8.3}$$
(pure substance, P=1)

and

$$\left(\frac{\partial\mu}{\partial p}\right)_T = V_{\text{m}} \tag{7.8.4}$$
(pure substance, P=1)

Since V_{m} is positive, Eq. 7.8.4 shows that the chemical potential increases with increasing pressure in an isothermal process.

The **standard chemical potential**, μ°, of a pure substance in a given phase and at a given temperature is the chemical potential of the substance when it is in the standard state of the phase at this temperature and the standard pressure p°.

There is no way we can evaluate the absolute value of μ at a given temperature and pressure, or of μ° at the same temperature—at least not to any useful degree of precision. The values of μ and μ° include the molar internal energy whose absolute value can only be calculated from the Einstein relation; see Sec. 2.6.2. We can however measure or calculate the *difference* $\mu - \mu^\circ$. The general procedure is to integrate $\text{d}\mu = V_{\text{m}}\,\text{d}p$ (Eq. 7.8.2 with $\text{d}T$ set equal to zero) from the standard state at pressure p° to the experimental state at pressure p':

$$\mu(p') - \mu^\circ = \int_{p^\circ}^{p'} V_{\text{m}}\,\text{d}p \tag{7.8.5}$$
(constant T)

7.8.1 Gases

For the standard chemical potential of a gas, this e-book will usually use the notation $\mu^\circ(\text{g})$ to emphasize the choice of a *gas* standard state.

An *ideal gas* is in its standard state at a given temperature when its pressure is the standard pressure. We find the relation of the chemical potential of an ideal gas to its pressure and its standard chemical potential at the same temperature by setting V_{m} equal to RT/p in Eq. 7.8.5: $\mu(p') - \mu^\circ = \int_{p^\circ}^{p'} (RT/p)\,\text{d}p = RT\ln(p'/p^\circ)$. The general relation for μ as a function of p, then, is

$$\mu = \mu^\circ(\text{g}) + RT\ln\frac{p}{p^\circ} \tag{7.8.6}$$
(pure ideal gas, constant T)

This function is shown as the dashed curve in Fig. 7.6.

If a gas is *not* an ideal gas, its standard state is a hypothetical state. The **fugacity**, f, of a real gas (a gas that is not necessarily an ideal gas) is defined by an equation with the same form as Eq. 7.8.6:

$$\mu=\mu^{\circ}(\mathrm{g})+RT\ln\frac{f}{p^{\circ}} \tag{7.8.7}$$
(pure gas)

or

$$f \overset{\text{def}}{=} p^{\circ}\exp\left[\frac{\mu-\mu^{\circ}(\mathrm{g})}{RT}\right] \tag{7.8.8}$$
(pure gas)

Note that fugacity has the dimensions of pressure. Fugacity is a kind of effective pressure. Specifically, it is the pressure that the hypothetical ideal gas (the gas with intermolecular forces “turned off”) would need to have in order for its chemical potential at the given temperature to be the same as the chemical potential of the real gas (see point C in Fig. 7.6). If the gas is an ideal gas, its fugacity is equal to its pressure.

To evaluate the fugacity of a real gas at a given T and p, we must relate the chemical potential to the pressure–volume behavior. Let μ' be the chemical potential and f' be the fugacity at the pressure p' of interest; let μ'' be the chemical potential and f'' be the fugacity of the same gas at some low pressure p'' (all at the same temperature). Then we use Eq. 7.8.5 to write $\mu'-\mu^{\circ}(\mathrm{g})=RT\ln(f'/p^{\circ})$ and $\mu''-\mu^{\circ}(\mathrm{g})=RT\ln(f''/p^{\circ})$, from which we obtain

$$\mu'-\mu''=RT\ln\frac{f'}{f''} \tag{7.8.9}$$

By integrating $\mathrm{d}\mu=V_{\mathrm{m}}\,\mathrm{d}p$ from pressure p'' to pressure p', we obtain

$$\mu'-\mu''=\int_{\mu''}^{\mu'}\mathrm{d}\mu=\int_{p''}^{p'}V_{\mathrm{m}}\,\mathrm{d}p \tag{7.8.10}$$

Equating the two expressions for $\mu'-\mu''$ and dividing by RT gives

$$\ln\frac{f'}{f''}=\int_{p''}^{p'}\frac{V_{\mathrm{m}}}{RT}\,\mathrm{d}p \tag{7.8.11}$$

In principle, we could use the integral on the right side of Eq. 7.8.11 to evaluate f' by choosing the lower integration limit p'' to be such a low pressure that the gas behaves as an ideal gas and replacing f'' by p''. However, because the integrand V_{m}/RT becomes very large at low pressure, the integral is difficult to evaluate. We avoid this difficulty by subtracting from the preceding equation the identity

$$\ln\frac{p'}{p''}=\int_{p''}^{p'}\frac{\mathrm{d}p}{p} \tag{7.8.12}$$

which is simply the result of integrating the function $1/p$ from p'' to p'. The result is

$$\ln\frac{f'p''}{f''p'}=\int_{p''}^{p'}\left(\frac{V_{\mathrm{m}}}{RT}-\frac{1}{p}\right)\mathrm{d}p \tag{7.8.13}$$

Now we take the limit of both sides of Eq. 7.8.13 as p'' approaches zero. In this limit, the gas at pressure p'' approaches ideal-gas behavior, f'' approaches p'', and the ratio $f'p''/f''p'$ approaches f'/p':

$$\ln\frac{f'}{p'}=\int_{0}^{p'}\left(\frac{V_{\mathrm{m}}}{RT}-\frac{1}{p}\right)\mathrm{d}p \tag{7.8.14}$$

The integrand $(V_{\mathrm{m}}/RT-1/p)$ of this integral approaches zero at low pressure, making it feasible to evaluate the integral from experimental data.

The **fugacity coefficient** ϕ of a gas is defined by

$$\phi \overset{\text{def}}{=} \frac{f}{p} \quad \text{or} \quad f=\phi p \tag{7.8.15}$$
(pure gas)

The fugacity coefficient at pressure p' is then given by Eq. 7.8.14:

$$\ln \phi(p') = \int_0^{p'} \left(\frac{V_\mathrm{m}}{RT} - \frac{1}{p} \right) \mathrm{d}p \tag{7.8.16}$$
(pure gas, constant T)

The isothermal behavior of real gases at low to moderate pressures (up to at least 1 bar) is usually adequately described by a two-term equation of state of the form given in Eq. 2.2.8:

$$V_\mathrm{m} \approx \frac{RT}{p} + B \tag{7.8.17}$$

Here B is the second virial coefficient, a function of T. With this equation of state, Eq. 7.8.16 becomes

$$\ln \phi \approx \frac{Bp}{RT} \tag{7.8.18}$$

For a real gas at temperature T and pressure p, Eq. 7.8.16 or 7.8.18 allows us to evaluate the fugacity coefficient from an experimental equation of state or a second virial coefficient. We can then find the fugacity from $f = \phi p$.

> As we will see in Sec. 9.7, the dimensionless ratio $\phi = f/p$ is an example of an *activity coefficient* and the dimensionless ratio f/p° is an example of an *activity*.

7.8.2 Liquids and solids

The dependence of the chemical potential on pressure at constant temperature is given by Eq. 7.8.5. With an approximation of zero compressibility, this becomes

$$\mu \approx \mu^\circ + V_\mathrm{m}(p - p^\circ) \tag{7.8.19}$$
(pure liquid or solid, constant T)

5.3: The Gibbs-Duhem Equation

For a system at **equilibrium**, the Gibbs-Duhem equation must hold:

$$\sum_i n_i d\mu_i = 0 \tag{5.3.1}$$

This relationship places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities,

$$G_{tot} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields

$$dG_{tot} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

But dG can also be expressed as

$$dG = Vdp - sdT + \sum_i \mu_i dn_i$$

Setting these two expressions equal to one another

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i}$$

And after canceling terms, one gets

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{5.3.2}$$

For a system at constant temperature and pressure

$$Vdp - sdT = 0 \tag{5.3.3}$$

Substituting Equation 5.3.3 into 5.3.2 results in the **Gibbs-Duhem equation** (Equation 5.3.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium. So for a binary system, consisting of components A and B (the two most often studied compounds in all of chemistry)

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

5.4: Criterion for Phase Equilibrium

The thermodynamic criterion for phase equilibrium is simple. It is based upon the chemical potentials of the components in a system. For simplicity, consider a system with only one component. For the overall system to be in equilibrium, the chemical potential of the compound in each phase present must be the same. Otherwise, there will be some mass migration from one phase to another, decreasing the total chemical potential of the phase from which material is being removed, and increasing the total chemical potential of the phase into which the material is being deposited. So for each pair of phases present (α and β) the following must be true:

$$\mu_\alpha = \mu_\beta$$

Gibbs Phase Rule

The **Gibbs phase rule** describes the number of compositional and phase variables that can be varied freely for a system at equilibrium. For each phase present in a system, the mole fraction of all but one component can be varied independently. However, the relationship

$$\sum_i \chi_i = 1$$

places a constraint on the last mole fraction. As such, there are $C-1$ compositional degrees of freedom for each phase present, where C is the number of components in the mixture. Similarly, all but one of the chemical potentials of each phase present must be equal, leaving only one that can be varied independently, leading to $P-1$ thermodynamic constraints placed on each component. Finally, there are two state variables that can be varied (such as pressure and temperature), adding two additional degrees of freedom to the system. The net number of degrees of freedom is determined by adding all of the degrees of freedom and subtracting the number of thermodynamic constraints.

$$\begin{aligned} F &= 2 + P(C-1) - C(P-1) \\ &= 2 + PC - P - PC + C \\ &= 2 + C - P \end{aligned} \tag{5.4.1}$$

Equation 5.4.1 is the Gibbs phase rule.

✓ Example 5.4.1:

Show that the maximum number of phases that can co-exist at equilibrium for a single component system is $P = 3$.

Solution

The maximum number of components will occur when the number of degrees of freedom is zero.

$$\begin{aligned} 0 &= 2 + 1 - P \\ P &= 3 \end{aligned}$$

Note: This shows that there can never be a “quadruple point” for a single component system!

Because a system at its triple point has no degrees of freedom, the triple point makes a very convenient physical condition at which to define a temperature. For example, the International Practical Temperature Scale of 1990 (IPT-90) uses the triple points of hydrogen, neon, oxygen, argon, mercury, and water to define several low temperatures. (The calibration of a platinum resistance thermometer at the triple point of argon, for example, is described by Strouse (Strouse, 2008)). The advantage to using a triple point is that the compound sets both the temperature and pressure, rather than forcing the researcher to set a pressure and *then* measure the temperature of a phase change, introducing an extra parameter than can introduce uncertainty into the measurement.

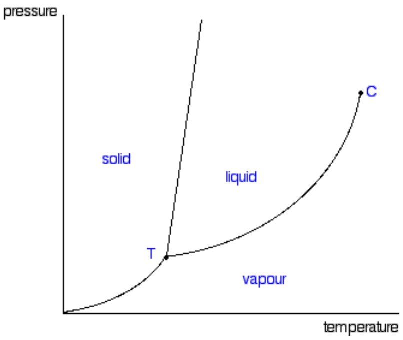
5.5: Phase Diagrams for Pure Substances

This page explains how to interpret the phase diagrams for simple pure substances - including a look at the special cases of the phase diagrams of water and carbon dioxide.

The Basic Phase Diagram

At its simplest, a phase can be just another term for solid, liquid or gas. If you have some ice floating in water, you have a solid phase present and a liquid phase. If there is air above the mixture, then that is another phase. But the term can be used more generally than this. For example, oil floating on water also consists of two phases - in this case, two liquid phases. If the oil and water are contained in a bucket, then the solid bucket is yet another phase. In fact, there might be more than one solid phase if the handle is attached separately to the bucket rather than molded as a part of the bucket.

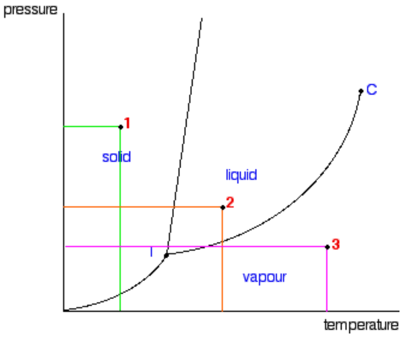
You can recognize the presence of the different phases because there is an obvious boundary between them - a boundary between the solid ice and the liquid water, for example, or the boundary between the two liquids. A *phase diagram* lets you work out exactly what phases are present at any given temperature and pressure. In the cases we'll be looking at on this page, the phases will simply be the solid, liquid or vapor (gas) states of a pure substance. This is the phase diagram for a typical pure substance.



These diagrams (including this one) are nearly always drawn highly distorted in order to see what is going on more easily. There are usually two major distortions. We'll discuss these when they become relevant. If you look at the diagram, you will see that there are three lines, three areas marked "solid", "liquid" and "vapor", and two special points marked "C" and "T".

The Three Areas

These are easy! Suppose you have a pure substance at three different sets of conditions of temperature and pressure corresponding to 1, 2 and 3 in the next diagram.

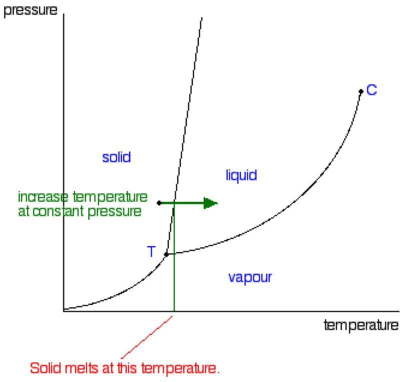


Under the set of conditions at 1 in the diagram, the substance would be a solid because it falls into that area of the phase diagram. At 2, it would be a liquid; and at 3, it would be a vapor (a gas).

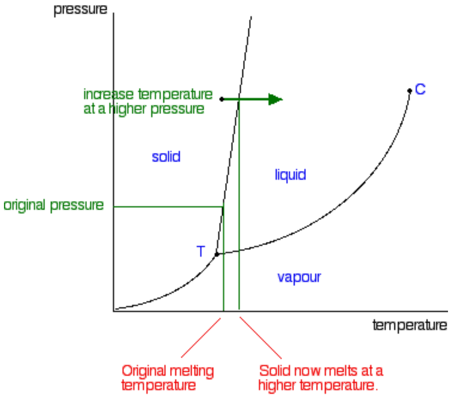
Phase Transitions

Moving from solid to liquid by changing the temperature

Suppose you had a solid and increased the temperature while keeping the pressure constant - as shown in the next diagram. As the temperature increases to the point where it crosses the line, the solid will turn to liquid. In other words, it melts.

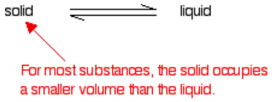


If you repeated this at a higher fixed pressure, the melting temperature would be higher because the line between the solid and liquid areas slopes slightly forward.



So what actually is this line separating the solid and liquid areas of the diagram?

It simply shows the effect of pressure on melting point. Anywhere on this line, there is an equilibrium between solid and liquid. You can apply Le Chatelier's Principle to this equilibrium just as if it was a chemical equilibrium. If you increase the pressure, the equilibrium will move in such a way as to counter the change you have just made.

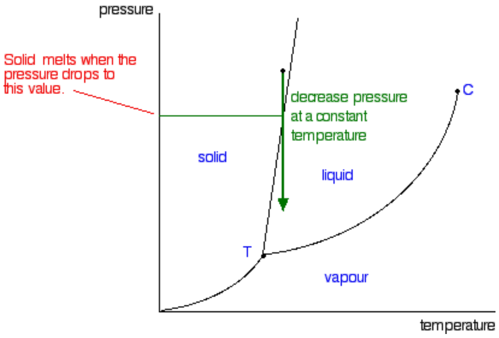


If it converted from liquid to solid, the pressure would tend to decrease again because the solid takes up slightly less space for most substances. That means that increasing the pressure on the equilibrium mixture of solid and liquid at its original melting point will convert the mixture back into the solid again. In other words, it will no longer melt at this temperature.

To make it melt at this higher pressure, you will have to increase the temperature a bit. Raising the pressure raises the melting point of most solids. That's why the melting point line slopes forward for most substances.

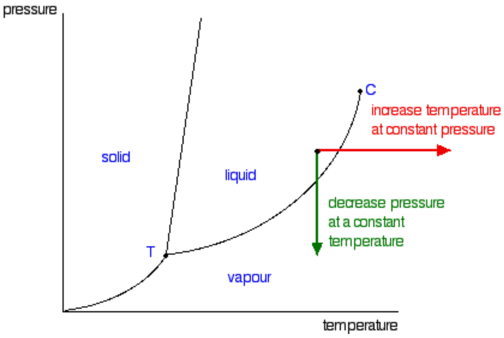
Moving from solid to liquid by changing the pressure

You can also play around with this by looking at what happens if you decrease the pressure on a solid at constant temperature.



Moving from liquid to vapor

In the same sort of way, you can do this either by changing the temperature or the pressure.

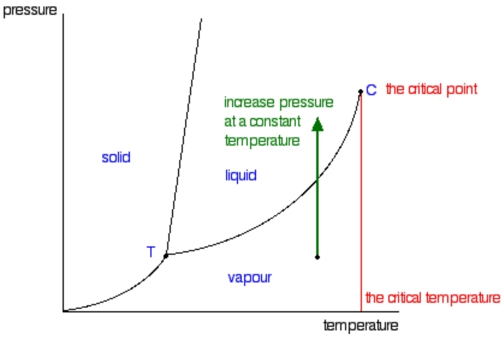


The liquid will change to a vapor - it boils - when it crosses the boundary line between the two areas. If it is temperature that you are varying, you can easily read off the boiling temperature from the phase diagram. In the diagram above, it is the temperature where the red arrow crosses the boundary line.

So, again, what is the significance of this line separating the two areas? Anywhere along this line, there will be an equilibrium between the liquid and the vapor. The line is most easily seen as the effect of pressure on the boiling point of the liquid. As the pressure increases, so the boiling point increases.

The critical point

You will have noticed that this liquid-vapor equilibrium curve has a top limit (labeled as **C** in the phase diagram), which is known as the *critical point*. The temperature and pressure corresponding to this are known as the critical temperature and critical pressure. If you increase the pressure on a gas (vapor) at a temperature lower than the critical temperature, you will eventually cross the liquid-vapor equilibrium line and the vapor will condense to give a liquid.

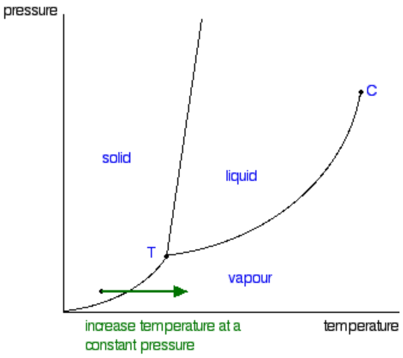


This works fine as long as the gas is below the critical temperature. What, though, if your temperature was above the critical temperature? There wouldn't be any line to cross! That is because, above the critical temperature, it is impossible to condense a gas into a liquid just by increasing the pressure. All you get is a highly compressed gas. The particles have too much energy for the intermolecular attractions to hold them together as a liquid. The critical temperature obviously varies from substance to substance and depends on the strength of the attractions between the particles. The stronger the intermolecular attractions, the higher the critical temperature.

Moving from solid to vapor

There's just one more line to look at on the phase diagram. This is the line in the bottom left-hand corner between the solid and vapor areas. That line represents solid-vapor equilibrium. If the conditions of temperature and pressure fell exactly on that line, there would be solid and vapor in equilibrium with each other - the solid would be subliming. (Sublimation is the change directly from solid to vapor or vice versa without going through the liquid phase.)

Once again, you can cross that line by either increasing the temperature of the solid, or decreasing the pressure. The diagram shows the effect of increasing the temperature of a solid at a (probably very low) constant pressure. The pressure obviously has to be low enough that a liquid can't form - in other words, it has to happen below the point labelled as **T**.



You could read the sublimation temperature off the diagram. It will be the temperature at which the line is crossed.

The Triple Point

Point **T** on the diagram is called the triple point. If you think about the three lines which meet at that point, they represent conditions of:

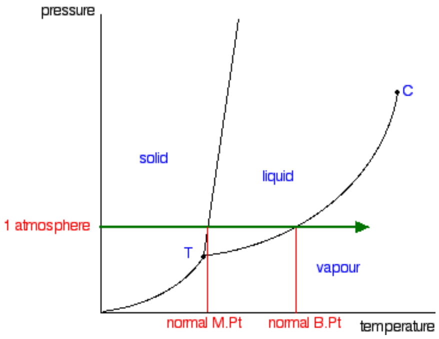
- solid-liquid equilibrium
- liquid-vapor equilibrium
- solid-vapor equilibrium

Where all three lines meet, you must have a unique combination of temperature and pressure where all three phases are in equilibrium together. That's why it is called a triple point.

If you controlled the conditions of temperature and pressure in order to land on this point, you would see an equilibrium which involved the solid melting and subliming, and the liquid in contact with it boiling to produce a vapor - and all the reverse changes happening as well. If you held the temperature and pressure at those values, and kept the system closed so that nothing escaped, that's how it would stay.

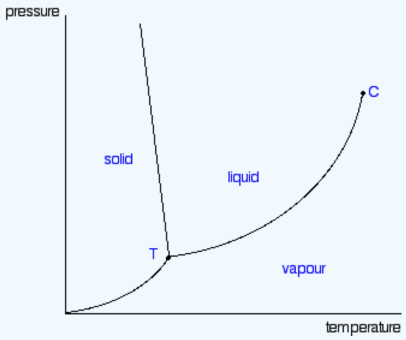
Normal melting and boiling points

The normal melting and boiling points are those when the pressure is 1 atmosphere. These can be found from the phase diagram by drawing a line across at 1 atmosphere pressure.

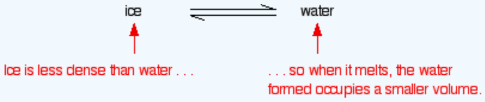


Example 5.5.1: Phase Diagram for Water

There is only one difference between this and the phase diagram that we've looked at up to now. The solid-liquid equilibrium line (the melting point line) slopes backwards rather than forwards.

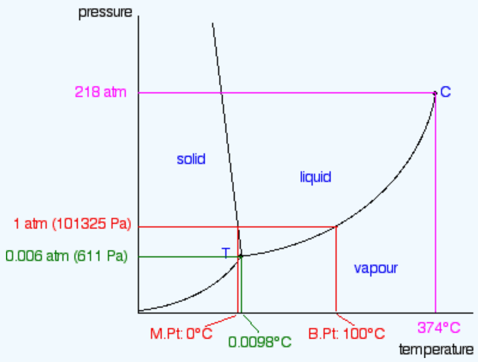


In the case of water, the melting point gets lower at higher pressures. Why?



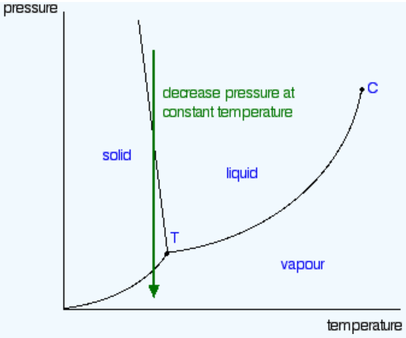
If you have this equilibrium and increase the pressure on it, according to Le Chatelier's Principle the equilibrium will move to reduce the pressure again. That means that it will move to the side with the smaller volume. Liquid water is produced. To make the liquid water freeze again at this higher pressure, you will have to reduce the temperature. Higher pressures mean lower melting (freezing) points.

Now lets put some numbers on the diagram to show the exact positions of the critical point and triple point for water.



Notice that the triple point for water occurs at a very low pressure. Notice also that the critical temperature is 374°C. It would be impossible to convert water from a gas to a liquid by compressing it above this temperature. The normal melting and boiling points of water are found in exactly the same way as we have already discussed - by seeing where the 1 atmosphere pressure line crosses the solid-liquid and then the liquid-vapor equilibrium lines.

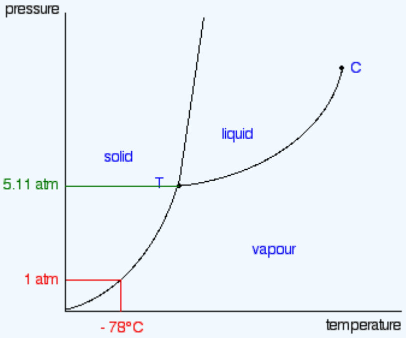
Just one final example of using this diagram. Imagine lowering the pressure on liquid water along the line in the diagram below.



The phase diagram shows that the water would first freeze to form ice as it crossed into the solid area. When the pressure fell low enough, the ice would then sublime to give water vapor. In other words, the change is from liquid to solid to vapor.

✓ Example $5.5.2$: Phase Diagram for Carbon Dioxide

The only thing special about this phase diagram is the position of the triple point which is well above atmospheric pressure. It is impossible to get any liquid carbon dioxide at pressures less than 5.11 atmospheres.



That means that at 1 atmosphere pressure, carbon dioxide will sublime at a temperature of -78°C. This is the reason that solid carbon dioxide is often known as "dry ice". You can't get liquid carbon dioxide under normal conditions - only the solid or the vapor.

Contributors and Attributions

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5.6: Gibbs Phase Rule

In chapter 1, we have already seen that the number of independent variables required to describe an ideal gas is two. This number was derived by counting the total number of variables $(3: P, \overline{V}, T)$, and reduce it by one because the ideal gas law constrains the value of one of them, once the other two are fixed. For a generic system potentially containing more than one chemical substance in several different phases, however, the number of independent variables can be different than two. For a system composed of c components (chemical substances) and p phases, the number of independent variables, f, is given by the Gibbs phase rule:

$$f = c - p + 2. \tag{5.6.1}$$

The Gibbs phase rule derives from the fact that different phases are in equilibrium with each other at some conditions, resulting in the reduction of the number of independent variables at those conditions. More rigorously, when two phases are in thermodynamic equilibrium, their chemical potentials are equal (see Equation 12.1.4). For each equality, the number of independent variables—also called the number of **degrees of freedom**—is reduced by one. For example, the chemical potentials of the liquid and its vapor depend on both T and P. But when these phases are in equilibrium with each other, their chemical potentials must be equal. If either the pressure or the temperature is fixed, the other variable will be uniquely determined by the equality relation. In other terms, when a liquid is in equilibrium with its vapor at a given pressure, the temperature is determined by the fact that the chemical potentials of the two phases is the same, and is denoted as the boiling temperature T_{b}. Similarly, at a given temperature, the pressure of the vapor is uniquely determined by the same equality relation and is denoted as the vapor pressure, P^*.

The Gibbs phase rule is obtained considering that the number of independent variables is given by the total number of variables minus the constraints. The total number of variables is given by temperature, pressure, plus all the variables required to describe each of the phases. The composition of each phase is determined by $(c-1)$ variables.[1] The number of constraints is determined by the number of possible equilibrium relations, which is $c(p-1)$ since the chemical potential of each component must be equal in all phases. The number of degrees of freedom f is then given by

$$\begin{aligned} f &= (c-1)p + 2 - c(p-1) \\ &= c - p + 2 \end{aligned}$$

which is the Gibbs phase rule, as in Equation 5.6.1.

---

1. For a 1-component system $c-1=1-1=0$, and no additional variable is required to determine the composition of each phase. For a 2-component system, however, each phase will contain both components, hence $c-1=2-1=1$ additional variable will be required to describe it–the mole fraction.

5.7: The Clapeyron Equation

Based on the thermodynamic criterion for equilibrium, it is possible to draw some conclusions about the state variables p and T and how they are related along phase boundaries. First, the chemical potentials of the two phases α and β in *equilibrium* with one another must be equal.

$$\mu_\alpha = \mu_\beta \tag{5.7.1}$$

Also, any infinitesimal changes to the chemical potential of one phase must be offset by an infinitesimal change to the chemical potential of the other phase that is equal in magnitude.

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta \tag{5.7.2}$$

Taking the difference between these Equations 5.7.1 and 5.7.2 shows that

$$d\mu_\alpha = d\mu_\beta$$

And since $d\mu$ can be expressed in terms of molar volume and molar entropy

$$d\mu = V dp - SdT$$

It is clear that there will be constraints placed on changes of temperature and pressure while maintaining equilibrium between the phases.

$$V_\alpha dP - S_\alpha dT = V_\beta dP - S_\beta dT$$

Gathering pressure terms on one side and temperature terms on the other

$$(V_\alpha - V_\beta)dP = (S_\alpha - S_\beta)dT$$

The differences $V_\alpha - V_\beta$ and $S_\alpha - S_\beta$ are the changes in molar volume and molar entropy for the phase changes respectively. So the expression can be rewritten

$$\Delta V dp = \Delta S dT$$

or

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \tag{5.7.3}$$

Equation 5.7.3 is the **Clapeyron equation**. This expression makes it easy to see how the phase diagram for water is qualitatively different than that for most substances. Specifically, the negative slope of the solid-liquid boundary on a pressure-temperature phase diagram for water is very unusual, and arises due to the fact that for water, the molar volume of the liquid phase is smaller than that of the solid phase.

Given that for a phase change

$$\Delta S_{phase} = \frac{\Delta H_{phase}}{T}$$

the Clapeyron equation is sometimes written

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \tag{5.7.4}$$

✓ Example 5.7.1: Freezing WAter

Calculate the magnitude of the change in freezing point for water ($\Delta H_{fus} = 6.009\, kJ/mol$) and the density of ice is $\rho_{ice} = 0.9167\, g/cm^3$ while that for liquid water is $\rho_{liquid} = 0.9999\, g/cm^3$) for an increase in pressure of $1.00\, atm$ at $273\, K$.

Solution

The molar volume of ice is given by

$$\left(0.9167\ \frac{g}{cm^3}\right)\left(\frac{1\ mol}{18.016\ g}\right)\left(\frac{1000\ cm^3}{1\ L}\right)=50.88\ \frac{L}{mol}$$

The molar volume of liquid water at 0 °C is given by

$$\left(0.9999\ \frac{g}{cm^3}\right)\left(\frac{1\ mol}{18.016\ g}\right)\left(\frac{1000\ cm^3}{1\ L}\right)=55.50\ \frac{L}{mol}$$

So ΔV for the phase change of solid $\rightarrow$ liquid (which corresponds to an endothermic change) is

$$50.88\ \frac{L}{mol}-55.50\ \frac{L}{mol}=-4.62\ \frac{L}{mol}$$

To find the change in temperature, use the *Clapeyron Equation* (Equation 5.7.4) and separating the variables

$$dp=\frac{\Delta H_{fus}}{\Delta V}\frac{dt}{T}$$

Integration (with the assumption that $\Delta H_{fus}/\Delta V$ does not change much over the temperature range) yields

$$\int_{p1}^{p2}dp=\frac{\Delta H_{fus}}{\Delta V}\int_{T1}^{T2}\frac{dt}{T}$$

$$p_2-p_1=\Delta p=\frac{\Delta H_{fus}}{\Delta V}\ln\left(\frac{T_2}{T_1}\right)$$

or

$$T_2=T_1\exp\left(\frac{\Delta V\Delta p}{\Delta H_{fus}}\right)$$

so

$$T_2=(273\ K)\exp\left(\frac{(1\ atm)\left(-4.62\ \frac{L}{mol}\right)}{6009\frac{J}{mol}}\underbrace{\left(\frac{8.314\ J}{0.08206\ atm\ L}\right)}_{\text{conversion factor}}\right)$$

$$T_2=252.5\ K$$

$$\Delta T=T_2-T_1=252.5\ K-273\ K=-20.5\ K$$

So the melting point will decrease by 20.5 K. Note that the phase with the smaller molar volume is favored at the higher pressure (as expected from Le Chatelier's principle)!

5.8: The Clausius-Clapeyron Equation

The Clapeyron equation can be developed further for phase equilibria involving the gas phase as one of the phases. This is the case for either sublimation (solid → gas) or vaporization (liquid → gas). In the case of vaporization, the change in molar volume can be expressed

$$\Delta V = V_{gas} - V_{liquid}$$

Since substances undergo a very large increase in molar volume upon vaporization, the molar volume of the condensed phase (liquid in this case) is negligibly small compared to the molar volume of the gas (i.e., $V_{gas} \gg V_{liquid}$). So,

$$\Delta V \approx V_{gas}$$

And if the vapor can be treated as an ideal gas,

$$V_{gas} = \frac{RT}{p}$$

Substitution into the Claperyron equation yields

$$\frac{dp}{dT} = \frac{p\Delta H_{vap}}{RT^2}$$

Separating the variables puts the equation into an integrable form.

$$dp = \frac{p\Delta H_{vap}}{R}\frac{dT}{T^2} \tag{5.8.1}$$

Noting that

$$\frac{dT}{T^2} = -d\left(\frac{1}{T}\right)$$

makes the integration very easy. If the enthalpy of vaporization is *independent* of temperature over the range of conditions,

$$\int_{p_1}^{p_2}\frac{dp}{p} = -\frac{\Delta H_{vap}}{R}\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.8.2}$$

This is the *Clausius-Clapeyron equation*. It can also be used to describe the boundary between solid and vapor phases by substituting the enthalpy of sublimation (ΔH_{sub})

✓ Example 5.8.1

The vapor pressure of a liquid triples when the temperature is increased from 25 °C to 45 °C. What is the enthalpy of vaporization for the liquid?

Solution

The problem can be solved using the Clausius-Clapeyron equation (Equation 5.8.2). The following values can be used:

$p_2 = 3p_1$	$T_2 = 318\,K$
$p_1 = p_1$	$T_1 = 298\,K$

Substitution into the Clausius-Clapeyron equation yields

$$\ln\left(\frac{3p_1}{p_1}\right) = -\frac{\Delta H_{vap}}{9.314\frac{J}{mol\,K}}\left(\frac{1}{318\,K} - \frac{1}{298\,K}\right)$$

$$\Delta H_{vap} = 43280\,\frac{J}{mol} = 43.28\,\frac{kJ}{mol}$$

The Clausius-Clapeyron equation also suggests that a plot of $\ln(p)$ vs. $1/T$ should yield a straight line, the slope of which is $-\Delta H/R$ (provided that ΔH_{vap} is independent of temperature over the range of temperatures involved..

$$\ln(p) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + const.$$

This approach in Example 5.8.1 is very useful when there are several pairs of measurements of vapor pressure and temperature. Such a plot is shown below for water.

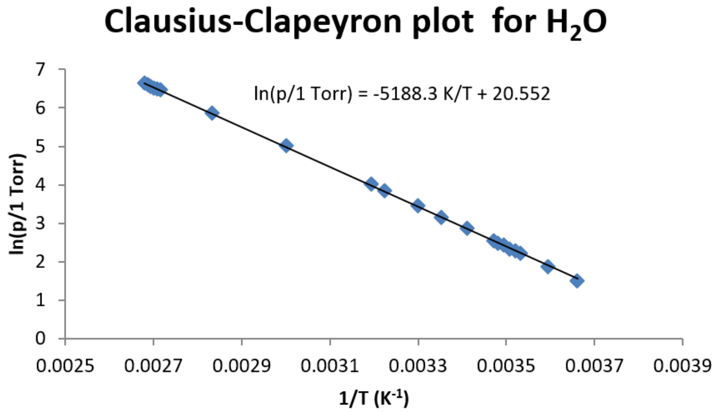


Figure 5.8.1

For water, which has a very large temperature dependence, the linear relationship of $\ln(p)$ vs. $1/T$ holds fairly well over a broad range of temperatures. So even though there is some curvature to the data, a straight line fit still results in a reasonable description of the data (depending, of course, on the precision needed in the experiment.) For this fit of the data, ΔH_{vap} is found to be 43.14 kJ/mol.

Temperature Dependence to ΔH_{vap}

For systems that warrant it, temperature dependence of ΔH_{vap} can be included into the derivation of the model to fit vapor pressure as a function of temperature. For example, if the enthalpy of vaporization is assumed to take the following empirical form

$$\Delta H_{vap} = \Delta H_o + aT + bT^2$$

and substituting it into the differential form of the Clausius-Clapeyron equation (Equation 5.8.1) generates

$$\frac{dp}{p} = \frac{\Delta H_o + aT + bT^2}{R}\frac{dT}{T^2}$$

or

$$\frac{dp}{p} = \frac{\Delta H_o}{R}\frac{dT}{T^2} + \frac{a}{R}\frac{dT}{T} + \frac{b}{R}dT$$

And so the integrated form becomes

$$\ln(p) = -\frac{\Delta H_o}{R}\left(\frac{1}{T}\right) + \frac{a}{R}\ln T + \frac{b}{R}T + constant$$

The results of fitting these data to the temperature dependent model are shown in the table below.

ΔH_0 (J mol^{-1})	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c
43080	0.01058	0.000501	20.50

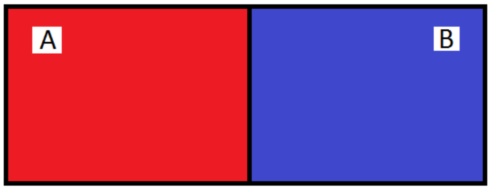
This results in calculated values of ΔH_{vap} of 43.13 kJ/mol at 298 K, and 43.15 kJ/mol at 373 K. The results are a little bit skewed since there is no data above 100 °C included in the fit. A larger temperature dependence would be found if the higher-temperature data were included in the fit.

CHAPTER OVERVIEW

6: Multiple Component Phase Equilibrium

6.1: Thermodynamics of Mixing

A natural place to begin a discussion of mixtures is to consider a mixture of two gases. Consider samples of the two gases filling two partitions in a single container, both at the same pressure, temperature, having volumes V_A and V_B.



After being allowed to mix isothermally, the partial pressures of the two gases will drop by a factor of 2 (although the total pressure will still be the original value) and the volumes occupied by the two gases will double.

Enthalpy of Mixing

Assuming ideal behavior, so that interactions between individual gas molecules are unimportant, it is fairly easy to calculate \(Delta H) for each gas, as it is simply an isothermal expansion. The total enthalpy of mixing is then given by

$$\Delta H_{mix} = \Delta H_A + \Delta H_B$$

And since the enthalpy change for an **isothermal expansion of an ideal gas is zero**,

$$\Delta H_{mix} = 0$$

is a straight-forward conclusion. This will be the criterion for an **ideal mixture**.

In general, real mixtures will deviate from this limiting ideal behavior due to interactions between molecules and other concerns. Also, many substances undergo chemical changes when they mix with other substances. But for now, we will limit ourselves to discussing mixtures in which no chemical reactions take place.

Entropy of Mixing

The entropy change induced due to isothermal mixing (assuming again no interactions between the molecules in the gas mixture) is again going to be the sum of the contributions from isothermal expansions of the two gases. Fortunately, entropy changes for isothermal expansions are easy to calculate for ideal gases.

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

If we use the initial volumes V_A and V_B for the initial volumes of gases A and B, the total volume after mixing is $V_A + V_B$, and the total entropy change is

$$\Delta S_{mix} = n_A R\ln\left(\frac{V_A + V_B}{V_A}\right) + n_A R\ln\left(\frac{V_A + V_B}{V_B}\right)$$

Noting that the term

$$\frac{V_A + V_B}{V_A} = \frac{1}{\chi_A}$$

where χ_A is the mole fraction of A after mixing, and that n_A can be expresses as the product of χ_A and the total number of moles, the expression can be rewritten

$$\Delta S_{mix} = n_{tot} R\left[-\chi_A \ln(\chi_A) - \chi_B \ln(\chi_B)\right]$$

It should be noted that because the mole fraction is always between 0 and 1, that $\ln(\chi_B) < 0$. As such, the entropy change for a system undergoing isothermal mixing is always positive, as one might expect (since mixing will make the system less ordered).

> *The entropy change for a system undergoing isothermal mixing is always positive.*

Free Energy of Mixing

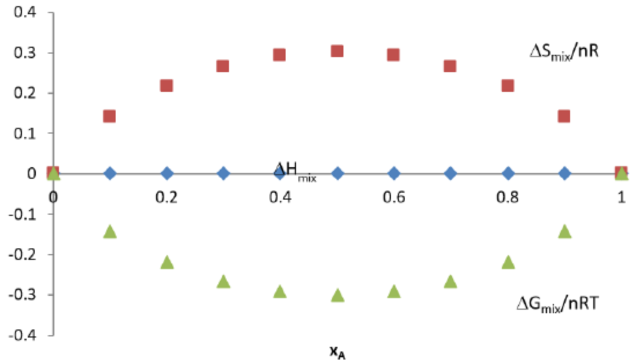
Calculating ΔG_{mix} should be no more difficult than calculating ΔS_{mix}. For *isothermal mixing* and constant total pressure

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

and so it follows from above that for the isothermal mixing of two gases at constant total pressure

$$\Delta G_{mix} = n_{tot} RT\left[-\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)\right]$$

The relationships describing the isothermal mixing of two ideal gases A and B is summarized in the graph below.



Again, because $\ln(\chi_i) < 0$, then $\Delta G_{mix} < 0$ implying that mixing is **always** a spontaneous process for an *ideal solution*. This is true for gases. But for many combinations of liquids or solids, the strong intermolecular forces may make mixing unfavorable (for example in the case of vegetable oil and water). Also, these interactions may make the volume non-additive as well (as in the case of ethanol and water).

> *Mixing is always a spontaneous process for an ideal solution.*

6.2: Partial Molar Volume

The **partial molar volume** of compound A in a mixture of A and B can be defined as

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B}$$

Using this definition, a change in volume for the mixture can be described using the total differential of V:

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B$$

or

$$dV = V_a\, dn_A + V_b\, dn_B$$

and integration yields

$$V = \int_0^{n_A} V_a\, dn_A + \int_0^{n_B} V_b\, dn_B$$

$$V = V_a\, n_A + V_b\, n_B$$

This result is important as it demonstrates an important quality of partial molar quantities. Specifically, if ξ_i represents the partial molar property X for component i of a mixture, The total property X for the mixture is given by

$$X = \sum_i \xi_i n_i$$

It should be noted that while the volume of a substance is never negative, the partial molar volume can be. An example of this appears in the dissolution of a strong electrolyte in water. Because the water molecules in the solvation sphere of the ions are physically closer together than they are in bulk pure water, there is a volume decrease when the electrolyte dissolves. This is easily observable at high concentrations where a larger fraction of the water in the sample is tied up in solvation of the ions.

6.3: Chemical Potential

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound i in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j\neq i} \tag{6.3.1}$$

This particular partial molar function is of particular importance, and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. And since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function. In general, the total change in the Gibbs function (dG) can be calculated from

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_j\neq i} dn_i$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives as was done in Chapter 6:

$$dG = V dp - SdT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions U, H, A, or G:

Table 6.3.1: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions

$dU = TdS - pdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j\neq i}$
$dH = TdS - VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j\neq i}$
$dA = -pdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j\neq i}$
$dG = Vdp - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j\neq i}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function is the most commonly used, and perhaps the most useful (Equation 6.3.1). As the partial most Gibbs function, it is easy to show that

$$d\mu = V dp - SdT$$

where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

and so at constant temperature

$$\int_{\mu^o}^{\mu} d\mu = \int_{p^o}^{p} V\, dp \tag{6.3.2}$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., κ_T is very small), therefore Equation 6.3.2 becomes

$$\int_{\mu^o}^{\mu} d\mu = V \int_{p^o}^{p} dp$$

$$\mu - \mu^o = V(p - p^o)$$

or

$$\mu = \mu^o + V(p - p^o)$$

Where p^o is a reference pressure (generally the standard pressure of 1 atm) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas

$$V = \frac{RT}{p}$$

So at constant temperature, Equation 6.3.2 then becomes

$$\int_{\mu^o}^{\mu} d\mu = RT int_{p^o}^{p} \frac{dp}{p} \tag{6.3.3}$$

or

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

6.4: Non-ideality in Gases - Fugacity

The relationship for chemical potential

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

was derived assuming **ideal gas** behavior. But for real gases that deviate widely from ideal behavior, the expression has only limited applicability. In order to use the simple expression on real gases, a “fudge” factor is introduced called **fugacity**. Using fugacity instead of pressure, the chemical potential expression becomes

$$\mu = \mu^o + RT \ln\left(\frac{f}{f^o}\right)$$

where f is the fugacity. Fugacity is related to pressure, but contains all of the deviations from ideality within it. To see how it is related to pressure, consider that a change in chemical potential for a single component system can be expressed as

$$d\mu - V\,dp - S dT$$

and so

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V \tag{6.4.1}$$

Differentiating the expression for chemical potential above with respect to pressure at constant volume results in

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \left\{\frac{\partial}{\partial p}\left[\mu^o + RT \ln\left(\frac{f}{f^o}\right)\right]\right\}$$

which simplifies to

$$\left(\frac{\partial \mu}{\partial p}\right)_T = RT\left[\frac{\partial \ln(f)}{\partial p}\right]_T = V$$

Multiplying both sides by p/RT gives

$$\left[\frac{\partial \ln(f)}{\partial p}\right]_T = \frac{pV}{RT} = Z$$

where Z is the compression factor as discussed previously. Now, we can use the expression above to obtain the **fugacity coefficient** γ, as defined by

$$f = \gamma p$$

Taking the natural logarithm of both sides yields

$$\ln f = \ln \gamma + \ln p$$

or

$$\ln \gamma = \ln f - \ln p$$

Using some calculus and substitutions from above,

$$\begin{aligned} \int \left(\frac{\partial \ln \gamma}{\partial p}\right)_T dp &= \int \left(\frac{\partial \ln f}{\partial p} - \frac{\partial \ln p}{\partial p}\right)_T dp \\ &= \int \left(\frac{Z}{\partial p} - \frac{1}{\partial p}\right)_T dp \end{aligned}$$

Finally, integrating from 0 to p yields

$$\ln \gamma = \int_0^p \left(\frac{Z-1}{p}\right)_T dp$$

If the gas behaves ideally, $\gamma = 1$. In general, this will be the limiting value as $p \rightarrow 0$ since all gases behave ideal as the pressure approaches 0. The advantage to using the fugacity in this manner is that it allows one to use the expression

$$\mu = \mu^o + RT \ln\left(\frac{f}{f^o}\right)$$

to calculate the chemical potential, insuring that Equation 6.4.1 holds even for gases that deviate from ideal behavior!

6.5: A Mixture is a Combination of Two or More Substances

So far, we have only discussed systems that are comprised of one component. Because a lot of chemistry occurs in mixtures or produces a mixture, chemists need to consider the thermodynamics of mixtures. A mixture can consist of many different components, however, for the sake of simplicity, we will restrict ourselves for now to two-component mixtures. Two-component mixtures can consist of two gases, two liquids, two solids, or even a liquid and a gas.

6.5.1: Partial Quantities and Scaling

Let's consider a two-component system where the volume and number of moles are changing. For example, we could have a system of a certain size of 1 and reduce its size stepwise in successive steps by taking half of it and throwing the other half away. The number of moles of each component, n_1 and n_2, will change as the volume of the system, V, changes:

$$dn_1 = n_1 dV$$

$$dn_2 = n_2 dV$$

The extensive Gibbs free energy will be affected the same way:

$$dG = G dV$$

At constant T and P we can write:

$$dG = -\cancel{SdT} + V\cancel{dP} + \mu_1 dn_1 + \mu_2 dn_2$$

So:

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$GdV = \mu_1 n_1 dV + \mu_2 n_2 dV$$

If we integrate this from the original size, 1, down to 0 (or 0 to 1, it does not matter). We get:

$$\int_0^1 GdV = \int_0^1 \mu_1 n_1 dV + \int_0^1 \mu_2 n_2 dV$$

$$G\int_0^1 dV = \mu_1 n_1 \int_0^1 dV + \mu_2 n_2 \int_0^1 dV$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

By the same argument we have:

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

where $\bar{V}_i$ is the partial molar volume for component i. These partial molar volumes are generally a function of composition (and P, T) and have been tabulated for a number of liquid systems. They allow us to calculate the real volume of a binary mixture. Volumes are generally speaking ***not strictly additive***. This fact is typically ignored in volumetric analysis and the use of molarities. Fortunately the deviations are often negligible in dilute solutions.

For phase diagrams, molarity (moles per liter) is not a very suitable quantity to use for concentration due to its volume dependence. Usually we work with mole fractions or molalities (moles per kilogram), where there are no volume dependencies.

6.5.2: Gaseous Mixtures

Gases can always mix in any ratio and mixtures typically act close to ideal unless heavily compressed or brought to low temperatures. The only exception is if the gases react (e.g, HCl and NH_3). Gas molecules experience little interaction with each other and, therefore, it does not matter much whether the molecules are different or the same. The total pressure can be computed by adding the partial pressures of the two components (Dalton's Law of Partial Pressures):

$$P_{total} = P_1 + P_2 \tag{6.5.1}$$

6.5.3: Liquid Mixtures

There are binary liquid systems that are fully miscible and are said to act as *ideal solutions*. Liquid molecules typically experience *strong* interactions with their neighbors. For the solution to be ideal, the interactions must remain *equally strong* even when the neighboring substance is different. This means they must be chemically similar. For this reason, liquid binaries are often *not* ideal. The next nearest thing are **regular solutions**. Even these systems can display phase segregation and limited mutual solubilities at low temperatures. Many liquid-liquid binaries diverge from ideality even more than the regular solutions and many of them are hardly miscible at all.

Table 24.1.1: Solutions

Solution/mixture	Interactions	Miscibility
Ideal gas	none	complete
Ideal liquid	strong but similar	complete
Regular liquid	strong, modestly dissimilar	not always complete
Real liquid	often strongly dissimilar	partial or none

6.5.4: Solid Mixtures

Solid binaries tend to be even less miscible than liquid binaries to the point that immiscibility is the rule and miscibility is the exception. Even totally miscible systems like electrum (the alloys of silver and gold) are far from ideal.

Figure 24.1.1: Electrum coin of the Byzantine Emperor Alexius I Comnenus. (CC-BY-SA-3.0; Classical Numismatic Group, Inc. http://www.cngcoins.com)

Another point of practical (kinetic rather than thermodynamic) importance is that even if two compounds are able to form a homogeneous solid solution, it usually takes heating for prolonged periods to get them to mix because solid diffusion is typically very slow. Nevertheless, solid solubility is an important issue for many systems, particularly for metal alloys. Two molecular solid substances that differ vastly in shape, size, polarity and or hydrogen bonding (e.g. organic compounds) typically have *negligible* mutual solid solubility. The latter fact is frequently exploited in organic chemistry to purify compounds through recrystallization.

Note

Solid solutions are relatively infrequent and never ideal.

6.5.5: Ideal liquid/Ideal Gas Phase Diagrams

Let's mix two liquids together. Liquids typically have different boiling points, with one being more volatile than the other. The vapor pressure of a component scales simply with the equilibrium vapor pressure of the pure component. In the gas phase, ***Dalton's law*** is applicable:

$$y_i = \frac{P_i}{P_{total}} \tag{6.5.2}$$

This is a consequence of the fact that ideal gases do not interact. The latter implies that the total pressure is simply the sum of the partial ones:

$$P_{total} = \sum_i^N P_i$$

If the liquid solution is ideal, then the vapor pressure of both components follow ***Raoult's law***, which states that the equilibrium vapor pressure above the mixture is the equilibrium pressure of the pure component times the mole fraction:

$$P_i = x_i P_i^* \tag{6.5.3}$$

- P_i is the vapor pressure of component i in the mixture
- P_i^* is equilibrium vapor pressure of the pure component i.
- x_i is the mole fraction of i^{th} component in the liquid phase.

Note that values for pure components are typically indicated by adding an asterisk * superscript.

The idea behind Raoult's law is that if the interactions are similar, it is a matter of random chance which component sits at the interface at any given moment. The equilibrium vapor pressure has to do with the probability that a molecule escapes from the interface into the gas phase and is dependent on both the substances volatility and the number that cover the surface. This leads to Raoult's Law, where we must multiply the vapor pressure of the pure liquid (volatility) by the mole fraction (number on the surface).

Note: Applicability of Raoult's Law

Raoult's law seldom holds completely, which is more applicable if the two components are almost chemically identical like two isomers, e.g., 1-propanol and 2-propanol.

6.5.6: The Pressure Phase Diagram

If we assume that temperature is constant, we can plot the total pressure for both Dalton and Raoult's laws versus composition (of gas: y_1 and liquid: x_1 on the same axis).

Liquid Phase:

$$P_{total} = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* - x_1 (P_2^* - P_1^*) \tag{6.5.4}$$

Clearly this is a straight line going from P_2^* at $x = 0$ to P_1^* at $x = 1$.

However the composition of the vapor in equilibrium with a liquid at a given mole fraction x is *different* than that of the liquid. So y is not x. If we take Dalton's law (Equation 6.5.2) and substitute Raoult's Law (Equation 6.5.3) in the numerator and the straight line in the denominator we get:

$$y_1 = \frac{x_1 P_1^*}{P_2^* - x_1 (P_2^* - P_1^*)} \tag{6.5.5}$$

Exercise

Suppose $P_1^* = 50$ Torr and $P_2^* = 25$ Torr. If (X_1= 0.6\) what is the composition of the vapor?

We can rearrange Equations 6.5.4 and 6.5.5 to plot the total pressure as function of y_1:

$$P_{total} = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*) y_1} \tag{6.5.6}$$

This is *not* a straight line.

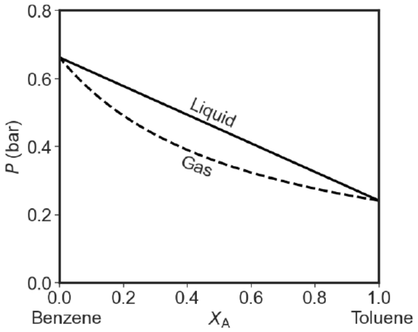


Figure 24.1.1: an ideal-ideal phase diagram for the binary system of toluene (A) and benzene (B). The curves are calculated from Equations 6.5.4 and 6.5.6.

As you can see when we plot both lines we get a diagram with three regions. At high pressures we just have a liquid. At low pressures we just have a gas. In between we have a ***phase gap*** or ***two phase region***. Points inside this region represent states that the system cannot achieve homogeneously. The horizontal ***tie-line*** shows which *two* phases coexists. I used the same 25 and 50 Torr values for the pure equilibrium pressures as in the question above. If you try to make a system with *overall* composition x and impose a pressure that falls in the forbidden zone you get two phases: a gaseous one that is richer in the more volatile component and a liquid one that is poorer in the volatile component than the overall composition would indicate.

6.5.7: The Temperature Phase Diagram

Note that the question: *what phase do we have when?* is really a function of ***both P and T***, so that if we want to represent *all* our knowledge in a diagram we should make it a three dimensional picture. This is not so easy to draw and not easy to comprehend visually either. This is why we usually look at a 2D cross section of the 3D space.

The above diagram is *isothermal*: we vary P, keeping T constant. It is, however, more usual (and easier) to do it the other way around. We keep pressure constant (say 1 bar, that's easy) and start heating things up isobarically.

The boiling points of our mixtures can also be plotted against x (the liquid composition) and y (the gaseous one) on the same horizontal axis. Again because in general y is not equal x we get two different curves. Neither of them are straight lines in this case and we end up with a lens-shaped two phase region:

binary T-X diagram showing the lever rule

binary T-X diagram showing the lever rule

What happens to a mixture with a given overall composition x(=x$_1$) when it is brought to a temperature where it boils can be seen at the intersection of a vertical line (an isopleth) at $x_{overall}$ and a horizontal one (an isotherm) at T_{boil}. If the intersection points in inside the two phase region a vapor phase and a liquid phase result that have a different composition from the overall one. The vapor phase is always richer in the more volatile component (the one with the lowest boiling point, on the left in the diagram). The liquid phase is enriched in the less volatile one.

6.5.7.1: The Lever Rule

How much of each phase is present is represented by the arrows in the diagram. The amount of liquid is proportional to the left arrow, the amount of gas to the right one (i.e. it works crosswise). The composition of the liquid in equilibrium with the vapor is:

$$x_2 = \frac{n_2^{liq}}{n_{1+2}^{liq}}$$

$$x_2^* n_{1+2}^{liq} = n_2^{liq}$$

The composition of the vapor is:

$$y_2 = \frac{n_2^{gas}}{n_{1+2}^{gas}}$$

$$y_2^* n_{1+2}^{gas} = n_2^{gas}$$

The overall composition is:

$$x_{all} = \frac{n_2^{liq+gas}}{n_{1+2}^{liq+gas}}$$

$$x^*_{all} n_{1+2}^{liq+gas} = n_2^{gas} + n_2^{liq}$$

$$x^*_{all} n_{1+2}^{liq+gas} = y^*_2 n_{1+2}^{gas} + x^*_2 n_{1+2}^{liq}$$

$$x^*_{all} n_{1+2}^{gas} + x^*_{all} n_{1+2}^{liq} = y^*_2 n_{1+2}^{gas} + x^*_2 n_{1+2}^{liq}$$

Thus:

$$\frac{n_{1+2}^{liq}}{n_{1+2}^{gas}} = \frac{y_2 - x_{all}}{x_{all} - x_2}$$

6.5.7.2: Distillation

The difference in composition between the gas and the liquid can be exploited to separate the two components, at least partially. We could trap the vapor and cool it down to form a liquid with a different composition. We could then boil it again and repeat the process. Each time the vapor will be more enriched in the volatile phase whereas the residual liquid is more enriched in the less volatile one. This process is known as ***distillation***. In practice the process is done one a fractionation column which makes it possible to have a series of vapor-liquid equilibria at once.

A good degree of purity can be reached this way, although 100% purity would take an infinite number of distillation steps.

6.6: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium

At **equilibrium**, there is no change in chemical potential for the system:

$$\sum_i n_i d\mu_i = 0 \tag{6.6.1}$$

This is the Gibbs-Duhem relationship and it places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities:

$$G_texttot = \sum_i n_i \mu_i \tag{6.6.2}$$

Taking the derivative of both sides yields:

$$dG_texttot = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \tag{6.6.3}$$

But dG can also be expressed as:

$$dG = Vdp - sdT + \sum_i \mu_i dn_i \tag{6.6.4}$$

Setting these two expressions equal to one another:

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i} \tag{6.6.5}$$

And after canceling terms, one gets:

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{6.6.6}$$

For a system at constant temperature and pressure:

$$Vdp - sdT = 0 \tag{6.6.7}$$

Substituting Equation 6.6.7 into 6.6.6 results in the **Gibbs-Duhem equation** (Equation 6.6.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium.

6.6.1: Gibbs-Duhem for Binary Systems

For a binary system consisting of components two components, A and B:

$$n_B d\mu_B + n_A d\mu_A = 0 \tag{6.6.8}$$

Rearranging:

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A \tag{6.6.9}$$

Consider a Gibbs free energy that only includes μ_n conjugate variables as we obtained it from our scaling experiment at T and P constant:

$$G = \mu_A n_A + \mu_B n_B$$

Consider a change in G:

$$dG = d(\mu_A n_A) + d(\mu_B n_B)$$

$$dG = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B$$

However, if we simply write out a change in G due to the number of moles we have:

$$dG = \mu_A dn_A + \mu_B dn_B$$

Consequently the other terms must add up to zero:

$$0 = n_A d\mu_A + n_B d\mu_B$$

$$d\mu_A = -\frac{n_B}{n_A} d\mu_B$$

$$d\mu_A = -\frac{x_B}{x_A} d\mu_B$$

In the last step we have simply divided both denominator and numerator by the total number of moles. This expression is the Gibbs-Duhem equation for a 2-component system. It relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

> *The Gibbs-Duhem equation relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).*

6.6.2: Gibbs-Duhem in the Ideal Case

In the ideal case we have:

$$\mu_B = \mu_B^* + RT \ln x_B$$

Gibbs-Duhem gives:

$$d\mu_A = -\frac{x_B}{x_A} d\mu_B$$

As:

$$d\mu_B = 0 + \frac{RT}{x_B}$$

with x_B being the only active variable at constant temperature, we get:

$$d\mu_A = -\frac{x_B}{x_A}\frac{RT}{x_B} = \frac{RT}{x_A}$$

If we now wish to find μ_A we need to integrate $d\mu_A$, e.g. form pure 1 to x_A. This produces:

$$\mu_A = \mu_A^* + RT \ln x_A$$

This demonstrates that Raoult's law can only hold over the whole range for one component ***if*** it also holds for the other over the whole range.

6.7: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound i in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i} \tag{6.7.1}$$

The partial molar function is of particular importance and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. Since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function and reach equilibrium. In general, the total change in the Gibbs function (dG) can be calculated from:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_j \neq i} dn_i \tag{6.7.2}$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives:

$$dG = VdP - SdT + \sum_i \mu_i dn_i \tag{6.7.3}$$

But as it turns out, the chemical potential can be defined as the partial molar quantity of any of the four major thermodynamic functions U, H, A, or G:

Table 6.7.1: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions

$dU = TdS - PdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq i}$
$dH = TdS - VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq i}$
$dA = -PdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j \neq i}$
$dG = VdP - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function, is the most commonly used, and perhaps the most useful (Equation 6.7.1). As the partial most Gibbs function, it is easy to show that:

$$d\mu = VdP - SdT \tag{6.7.4}$$

where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V \tag{6.7.5}$$

and so at constant temperature:

$$\int_{\mu^o}^{\mu} d\mu = \int_{P^o}^{P} V\, dP \tag{6.7.6}$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., κ_T is very small), therefore Equation 6.7.6 becomes:

$$\int_{\mu^o}^{\mu} d\mu = V \int_{P^o}^{P} dP \tag{6.7.7}$$

$$\mu - \mu^o = V(P - P^o) \tag{6.7.8}$$

or:

$$\mu = \mu^o + V(P - P^o) \tag{6.7.9}$$

Where P^o is the standard state pressure (1 bar) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas:

$$V = \frac{RT}{P} \tag{6.7.10}$$

So at constant temperature, Equation 6.7.6 then becomes:

$$\int_{\mu^o}^{\mu} d\mu = RTint_{P^o}^{P} \frac{dP}{P} \tag{6.7.11}$$

or:

$$\mu = \mu^o + RT \ln\left(\frac{P}{P^o}\right) \tag{6.7.12}$$

A lot of chemistry takes place in solution and therefore this topic is of prime interest for chemistry.

6.7.1: Thermodynamic potentials of solutions

The Gibbs free energy of an ideal gas depends logarithmically on pressure:

$$G = G^o + RT \ln \frac{P}{P^o}$$

P$^\ominus$ is *is often dropped out of the formula.* and we write:

$$G = G^o + RT \ln P$$

> Notice however that although P and P/P^o have the same numerical value, the dimensions are different. P usually has dimensions of bar, but P/P^o is *dimensionless*.

If we have a gas mixture we can hold the same logarithmic argument for each partial pressure as the gases do not notice each other. We do need to take into account the number of moles of each and work with (partial) molar values, i.e. the thermodynamic potential:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{6.7.13}$$

If we are dealing with an equilibrium over an ideal liquid solution the situation in the gas phase gives us a probe for the situation in the liquid. The equilibrium must hold for each of *all* components j (say two in binary mixture). That means that for each of them the thermodynamic potential in the liquid and in the gas must be equal:

$$\mu_j^{sln} = \mu_j^{gas}$$

for all j. Consider what happens to a pure component, e.g. $j = 1$ in equilibrium with its vapor. We can write:

$$\mu_1^{pure\ liq} = \mu_1^{pure\ vapor} = \mu_1^o + RT \ln \frac{P_1^*}{P^o}$$

The asterisk in P_1^* denotes the equilibrium vapor pressure of pure component 1 and we will use that to indicate the thermodynamic potential of pure compounds too:

$$\mu_1^{*liq} = \mu_1^o + RT \ln \frac{P_1^*}{P^o} \tag{6.7.14}$$

Combining Equations 6.7.14 and 6.7.13 we find a relationship between the solution and the pure liquid:

$$\mu_j^{sln} = \mu_j^* + RT \ln \frac{P_j}{P_j^*}$$

Notice that the *gas* and its pressure is used to link the mixture and the pure compound.

6.8: Colligative Properties

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

- **Solution** – a homogeneous mixture.
- **Solvent** – The component of a solution with the largest mole fraction
- **Solute** – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous (aerosols are examples of gas-phase solutions) forms. For the most part, this discussion will focus on liquid-phase solutions.

Freezing Point Depression

In general (and as will be discussed in Chapter 8 in more detail) a liquid will freeze when

$$\mu_{solid} \leq \mu_{liquid}$$

As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent. As it turns out, the chemical potential of the solvent is reduced by the presence of a solute.

In a mixture, the chemical potential of component A can be calculated by

$$\mu_A = \mu_A^o + RT\ln\chi_A \tag{6.8.1}$$

And because χ_A is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

The condition under which the solvent will freeze is

$$\mu_{A,solid} = \mu_{A,liquid}$$

where the chemical potential of the liquid is given by Equation 6.8.1, which rearrangement to

$$\frac{\mu_A - \mu_A^o}{RT} = \ln\chi_A$$

To evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_A - \mu_A^o}{RT}\right)\right]_p = \left(\frac{\partial \ln\chi_A}{\partial T}\right)_p$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT}\left[\left(\frac{\partial \mu_A}{\partial T}\right)_p - \left(\frac{\partial \mu_A^o}{\partial T}\right)_p\right] = \left(\frac{\partial \ln\chi_A}{\partial T}\right)_p \tag{6.8.2}$$

Recalling that

$$\mu = H = TS$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

Equation 6.8.2 becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT}[-S_A + S_A^o] = \left(\frac{\partial \ln\chi_A}{\partial T}\right)_p \tag{6.8.3}$$

And noting that in the case of the solvent freezing, H_A^o is the enthalpy of the pure solvent in solid form, and H_A is the enthalpy of the solvent in the liquid solution. So

$$H_A^o - H_a = \Delta H_{fus}$$

Equation 6.8.3 then becomes

$$\frac{\Delta H_{fus}}{RT^2} - \frac{-S_A + S_A^o}{\cancel{RT}} + \frac{-S_A + S_A^o}{\cancel{RT}} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

or

$$\frac{\Delta H_{fus}}{RT^2} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^{T} \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln \chi_A \tag{6.8.4}$$

where T^o is the freezing point of the pure solvent and T is the temperature at which the solvent will begin to solidify in the solution. After integration of Equation 6.8.4:

$$-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right) = \ln \chi_A \tag{6.8.5}$$

This can be simplified further by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o}$$

where ΔT is the difference between the freezing temperature of the pure solvent and that of the solvent in the solution. Also, for small deviations from the pure freezing point, TT^o can be replaced by the approximate value $(T^o)^2$. So the Equation 6.8.5 becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2} \Delta T = \ln \chi_A \tag{6.8.6}$$

Further, for dilute solutions, for which χ_A, the mole fraction of the solvent is very nearly 1, then

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

where χ_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{R(T^o)^2}{\Delta H_{fus}}\right) \chi_B$$

The first factor can be replaced by K_f:

$$\frac{R(T^o)^2}{\Delta H_{fus}} = K_f$$

which is the **cryoscopic constant** for the solvent.

ΔT gives the magnitude of the reduction of freezing point for the solution. Since ΔH_{fus} and T^o are properties of the solvent, the freezing point depression property is independent of the solute and is a property based solely on the nature of the solvent. Further, since χ_B was introduced as $(1 - \chi_A)$, it represents the sum of the mole fractions of all solutes present in the solution.

It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of ΔT will change as the freezing process continually removes solvent from the liquid phase of the solution.

Boiling Point Elevation

The derivation of an expression describing boiling point elevation is similar to that for freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, cause it to favor the liquid phase over the vapor phase. As sch, the temperature must be increased to increase the chemical potential of the solvent in the liquid solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b \chi_B$$

where

$$\frac{R(T^o)^2}{\Delta H_{vap}} = K_b$$

is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes. A very elegant derivation of the form of the models for freezing point depression and boiling point elevation has been shared by F. E. Schubert (Schubert, 1983).

Cryoscopic and ebullioscopic constants are generally tabulated using molality as the unit of solute concentration rather than mole fraction. In this form, the equation for calculating the magnitude of the freezing point decrease or the boiling point increase is

$$\Delta T = K_f\, m$$

or

$$\Delta T = K_b\, m$$

where m is the concentration of the solute in moles per kg of solvent. Some values of K_f and K_b are shown in the table below.

Substance	K_f (°C kg mol-1)	T_f^o (°C)	K_b (°C kg mol-1)	T_b^o (°C)
Water	1.86	0.0	0.51	100.0
Benzene	5.12	5.5	2.53	80.1
Ethanol	1.99	-114.6	1.22	78.4
CCl_4	29.8	-22.3	5.02	76.8

✓ Example 6.8.1:

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of CCl_4 raises the boiling point to 81.5 °C. What is the molar mass of the compound?

Solution

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(85.5\,^\circ C - 76.8\,^\circ C) = (5.02\,^\circ C\; Kg/mol)\, m$$

$$m = 0.936\, mol/kg$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\, mol/\,\cancel{kg}\right)(0.02\ \cancel{kg}) = 0.0234\, mol$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\, g}{0.0234} = 128 g/mol$$

Vapor Pressure Lowering

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{vapor} = \mu_{solvent}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu^o_{vap} + RT \ln \frac{p'}{p^o} = \mu^o_A + RT \ln \chi_A \tag{6.8.7}$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu^o_A = \mu^o_{vap} + RT \ln \frac{p_A}{p^o} \tag{6.8.8}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substituting Equation 6.8.8 into Equation 6.8.7 yields

$$\cancel{\mu^o_{vap}} + RT \ln \frac{p'}{p^o} = \left(\cancel{\mu^o_{vap}} + RT \ln \frac{p_A}{p^o} \right) + RT \ln \chi_A$$

The terms for μ^o_{vap} cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln \chi_A$$

Subtracting $RT \ln(P_A/P^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln \chi_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln \chi_A$$

Dividing both sides by RT and then exponentiating yields

$$\frac{p'}{p_A} = \chi_A$$

or

$$p' = \chi_A p_A \tag{6.8.9}$$

This last result is Raoult's Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

✓ Example 6.8.2:

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

Solution

Using Raoult's Law (Equation 6.8.9)

$$p_A = (0.400)(150\, Toor) = 60.0\, Torr$$

$$p_B = (0.600)(300\, Toor) = 180.0\, Torr$$

$$p_{tot} = p_A + p_B = 240\, Torr$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

$$\chi_A = \frac{p_A}{p_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

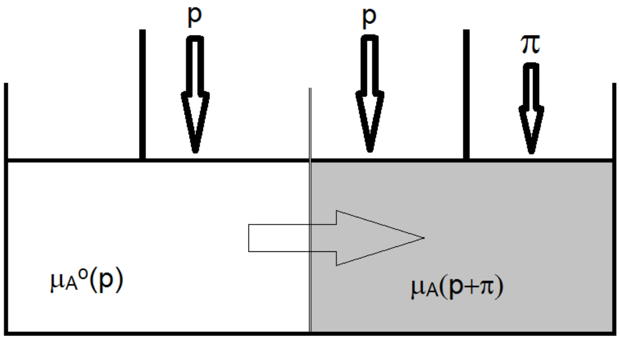
$$\chi_B = \frac{p_B}{p_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$\chi_A + \chi_B = 1$$

Osmotic Pressure

Osmosis is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln \chi_A$$

And since $x_A < 1$, the chemical potential is of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(\chi_b, +\pi)$$

To solve the problem to determine the magnitude of p, the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure p must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = RT \ln \chi_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p+\pi) = \mu(p) + \int_p^\pi \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

where V is the molar volume of the substance. Combining these expressions results in

$$-RT \ln \chi_A = \int_p^{p+\pi} V\, dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of κ_T – which is the case for most liquids) the term on the right becomes.

$$\int_p^{\pi} V\, dP = Vp|_p^{p+\pi} = V\pi$$

Also, for values of χ_A very close to 1

$$\ln \chi_A \approx -(1-\chi_A) = -\chi_B$$

So, for dilute solutions

$$\chi_B RT = V\pi$$

Or after rearrangement

$$\pi \frac{\chi_B RT}{V}$$

again, where V is the molar volume of the solvent. And finally, since χ_B/V is the concentration of the solute B for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure π is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

6.9: Osmotic Pressure can Determine Molecular Masses

Some membrane materials are permeable for some molecules, but not for others. This is often a matter of the *size* of the molecules, but it can also be a question of *solubility* of the molecule in the barrier material. Many biological membranes have semipermeable properties and osmosis is therefore an important biological process. Figure 25.4.1 shows a simple osmotic cell. Both compartments contain water, but the one on the right also contains a solute whose molecules (represented by green circles) are too large to pass through the membrane. Many artificial and natural substances are capable of acting as semi-permeable membranes. For example, the walls of most plant and animal cells fall into this category.

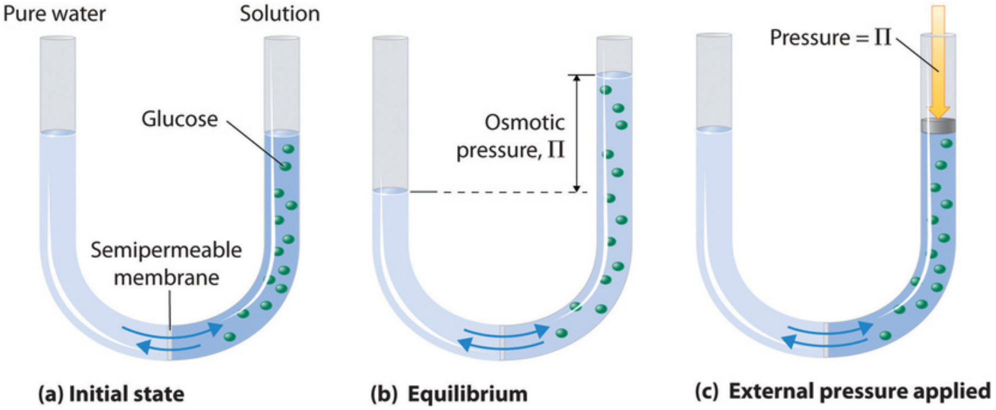


Figure 25.4.1 : Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

If solvent molecules can pass through the membrane, but solute molecules (or ions) cannot, solvent molecules will spontaneously migrate across the membrane to increase the solution's volume and thus reduce its concentration. If the solution is ideal, this process is in many ways analogous to the spontaneous increase in volume of a gas allowed to expand against vacuum. Of course the volume of the 'solute-gas' is limited by the availability of solvent and, if done under gravity in a U-shaped tube, by the build up of hydrostatic pressure. This pressure is known as the *osmotic pressure* Π. At equilibrium we can write:

$$\mu^*(T,P) = \mu^{sln}(T,P+\Pi,a_1)$$

$$\mu^*(T,P) = \mu^*(T,P+\Pi) + RT\ln a_1$$

From Gibbs energy (dG) in its natural variables (P,T) we know that:

$$\left(\frac{\partial G}{\partial P}\right)_{T,x} = V$$

Taking the partial versus x_1 we get:

$$\left(\frac{\partial \mu^*}{\partial P}\right)_{T,x_j} = \bar{V}_1^*$$

This means we can integrate over the molar volume to convert $\mu^*(T,P+\Pi)$ to a different pressure:

$$\mu^*(T,P+\Pi) = \mu^*(T,P) + \int_P^{P+\Pi} \bar{V}_1^* dP$$

Thus we get:

$$\mu^*(T,P) = \mu^*(T,P+\Pi) + RT\ln a_1$$

$$\mu^*(T,P) = \mu^*(T,P) + \Pi\bar{V}_1^* + RT\ln a_1$$

Once again using the ideal approximation:

$$\ln a_1 \ln x_1 \approx -x_2$$

we get:

$$RTx_2 = \Pi \bar{V}_1^*$$

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

The combination gives an expression involving the molarity:

$$\Pi = RTc$$

Where c is the molar concentration. Osmosis can be used in reverse, if we apply about 30 bar to sea water we can obtain fresh water on the other side of a suitable membrane. This process is used in some places, but better membranes would be desirable and they easily get clogged. The resulting water is not completely salt-free and this means that if used for agriculture the salt may accumulate on the field over time.

6.9.1: Determining Molar Masses

Both melting point depression and boiling point elevation only facilitate the determination of relatively *small* molar weights. The need for such measurements is no longer felt because we now have good techniques to determine the structure of most small to medium size molecules. For polymers this is a different matter. They usually have a molecular weight (mass) *distribution* and determining it is an important topic of polymer science.

Osmometry is still of some practical usefulness. It is also colligative and able to measure up to about 8000 daltons. Many polymers are much bigger than that. Their mass distribution is usually determined by different means. The polymers is dissolved and led over a chromatographic column usually based on size-exclusion. The effluent is then probed as function of the elution time by a combination of techniques:

1. UV absorption (determine the monomer concentration)
2. Low Angle Laser Light Scattering (LALLS) and/or Viscometry

The latter two provide information on the molar mass distribution but they give a different moment of that distribution. The combination of techniques gives an idea not only of how much material there is of a given molar mass but also of the linearity or degree of branching of the chains.

Purity analysis

Nevertheless melting point depression is still used in a somewhat different application. When a slightly impure solid is melted its melting point in depressed. Also the melting process is not sudden but takes place over the whole trajectory from typically a lower eutectic temperature up to the depressed melting point (the liquid line in the phase diagram). In organic synthesis the melting behavior is often used as a first convenient indication of purity. In a differential scanning calorimetry (DSC) experiment the melting peak becomes progressively skewed towards lower temperatures at higher impurity levels. The shape of the curve can be modeled with a modified version of the melting point depression expression. This yields a value for the total impurity level in the solid. This technique is used in the pharmaceutical industry for quality control purposes.

6.10: Raoult's Law and Phase Diagrams of Ideal Solutions

The behavior of the vapor pressure of an ideal solution can be mathematically described by a simple law established by François-Marie Raoult (1830–1901). **Raoult's law** states that the partial pressure of each component, i, of an ideal mixture of liquids, P_i, is equal to the vapor pressure of the pure component P_i^* multiplied by its mole fraction in the mixture x_i:

$$P_i = x_i P_i^*. \tag{6.10.1}$$

One volatile component

Raoult's law applied to a system containing only one volatile component describes a line in the Px_{B} plot, as in Figure $6.10.1$.

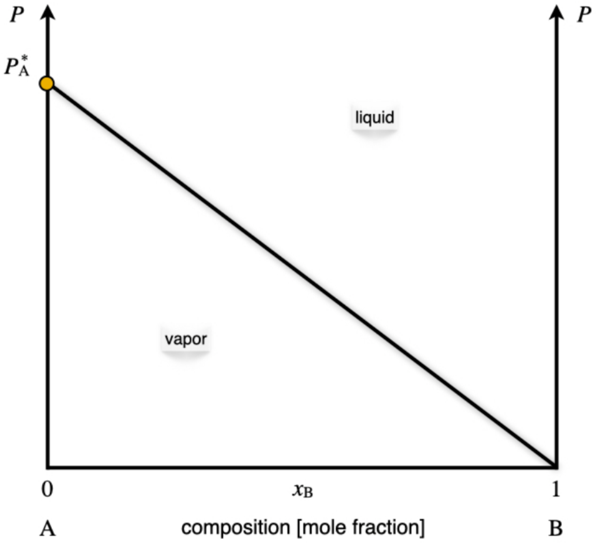


Figure 6.10.1: The Pressure–Composition Phase Diagram of an Ideal Solution Containing a Single Volatile Component at Constant Temperature.

As emerges from Figure $6.10.1$, Raoult's law divides the diagram into two distinct areas, each with three degrees of freedom.[1] Each area contains a phase, with the vapor at the bottom (low pressure), and the liquid at the top (high pressure). Raoult's law acts as an additional constraint for the points sitting on the line. Therefore, the number of independent variables along the line is only two. Once the temperature is fixed, and the vapor pressure is measured, the mole fraction of the volatile component in the liquid phase is determined.

Two volatile components

In an ideal solution, every volatile component follows Raoult's law. Since the vapors in the gas phase behave ideally, the total pressure can be simply calculated using Dalton's law as the sum of the partial pressures of the two components $P_{\text{TOT}} = P_{\text{A}} + P_{\text{B}}$. The corresponding diagram is reported in Figure $6.10.2$. The total vapor pressure, calculated using Dalton's law, is reported in red. The Raoult's behaviors of each of the two components are also reported using black dashed lines.

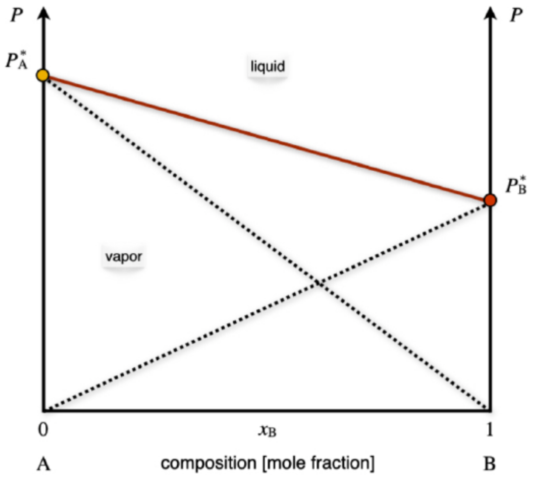


Figure 6.10.2: The Pressure–Composition Phase Diagram of an Ideal Solution Containing Two Volatile Components at Constant Temperature.

? Exercise 6.10.1

Calculate the mole fraction in the vapor phase of a liquid solution composed of 67% of toluene (A) and 33% of benzene (B), given the vapor pressures of the pure substances: $P_{\mathrm{A}}^* = 0.03$ bar, and $P_{\mathrm{B}}^* = 0.10$ bar.

Answer

The data available for the systems are summarized as follows:

$$\begin{aligned} x_{\mathrm{A}} &= 0.67 & x_{\mathrm{B}} &= 0.33 \\ P_{\mathrm{A}}^* &= 0.03 \text{ bar} & P_{\mathrm{B}}^* &= 0.10 \text{ bar} \\ & & P_{\mathrm{TOT}} = ? & \\ y_{\mathrm{A}} &= ? & y_{\mathrm{B}} &= ? \end{aligned} \tag{6.10.2}$$

The total pressure of the vapors can be calculated combining Dalton's and Roult's laws:

$$\begin{aligned} P_{\mathrm{TOT}} &= P_{\mathrm{A}} + P_{\mathrm{B}} = x_{\mathrm{A}} P_{\mathrm{A}}^* + x_{\mathrm{B}} P_{\mathrm{B}}^* \\ &= 0.67 \cdot 0.03 + 0.33 \cdot 0.10 \\ &= 0.02 + 0.03 = 0.05 \text{ bar} \end{aligned} \tag{6.10.3}$$

We can then calculate the mole fraction of the components in the vapor phase as:

$$\begin{aligned} y_{\mathrm{A}} &= \frac{P_{\mathrm{A}}}{P_{\mathrm{TOT}}} & y_{\mathrm{B}} &= \frac{P_{\mathrm{B}}}{P_{\mathrm{TOT}}} \\ y_{\mathrm{A}} &= \frac{0.02}{0.05} = 0.40 & y_{\mathrm{B}} &= \frac{0.03}{0.05} = 0.60 \end{aligned} \tag{6.10.4}$$

Notice how the mole fraction of toluene is much higher in the liquid phase, $x_{\mathrm{A}} = 0.67$, than in the vapor phase, $y_{\mathrm{A}} = 0.40$.

As is clear from the results of Exercise $6.10.1$, the concentration of the components in the gas and vapor phases are different. We can also report the mole fraction in the vapor phase as an additional line in the Px_{B} diagram of Figure $6.10.2$. When both concentrations are reported in one diagram—as in Figure $6.10.3$—the line where x_{B} is obtained is called the *liquidus line*, while the line where the y_{B} is reported is called the *Dew point line*.

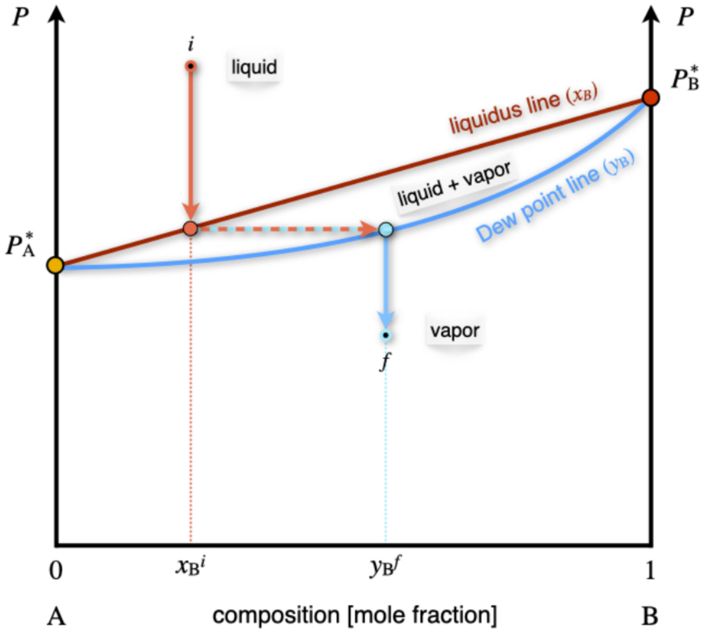


Figure 6.10.3: The Pressure–Composition Phase Diagram of an Ideal Solution Containing Two Volatile Components at Constant Temperature. Both the Liquidus and Dew Point Line are Emphasized in this Plot.

The liquidus and Dew point lines determine a new section in the phase diagram where the liquid and vapor phases coexist. Since the degrees of freedom inside the area are only 2, for a system at constant temperature, a point inside the coexistence area has fixed mole fractions for both phases. We can reduce the pressure on top of a liquid solution with concentration x_B^i (see Figure $6.10.3$) until the solution hits the liquidus line. At this pressure, the solution forms a vapor phase with mole fraction given by the corresponding point on the Dew point line, y_B^f.

T_B phase diagrams and fractional distillation

We can now consider the phase diagram of a 2-component ideal solution as a function of temperature at constant pressure. The T_B diagram for two volatile components is reported in Figure $6.10.4$.

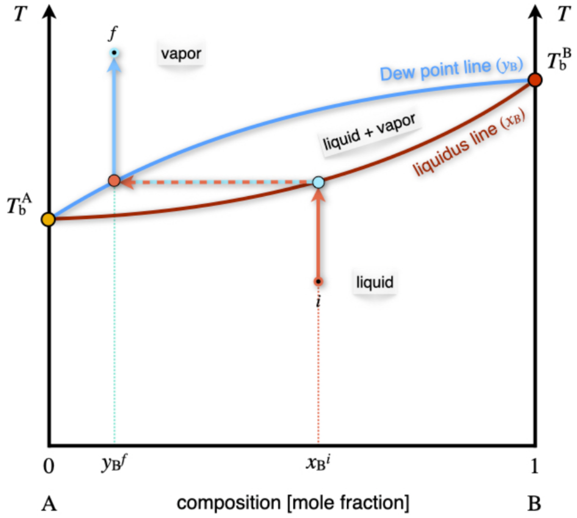


Figure 6.10.4: The Temperature–Composition Phase Diagram of an Ideal Solution Containing Two Volatile Components at Constant Pressure.

Compared to the Px_B diagram of Figure $6.10.3$, the phases are now in reversed order, with the liquid at the bottom (low temperature), and the vapor on top (high Temperature). The liquidus and Dew point lines are curved and form a lens-shaped region where liquid and vapor coexists. Once again, there is only one degree of freedom inside the lens. As such, a liquid solution of initial composition x_{B}^{i} can be heated until it hits the liquidus line. At this temperature the solution boils, producing a vapor with concentration y_{B}^{f}. As is clear from Figure $6.10.4$, the mole fraction of the B component in the gas phase is lower than the mole fraction in the liquid phase. This fact can be exploited to separate the two components of the solution. In particular, if we set up a series of consecutive evaporations and condensations, we can distill fractions of the solution with an increasingly lower concentration of the less volatile component B. This is exemplified in the industrial process of fractional distillation, as schematically depicted in Figure $6.10.5$.

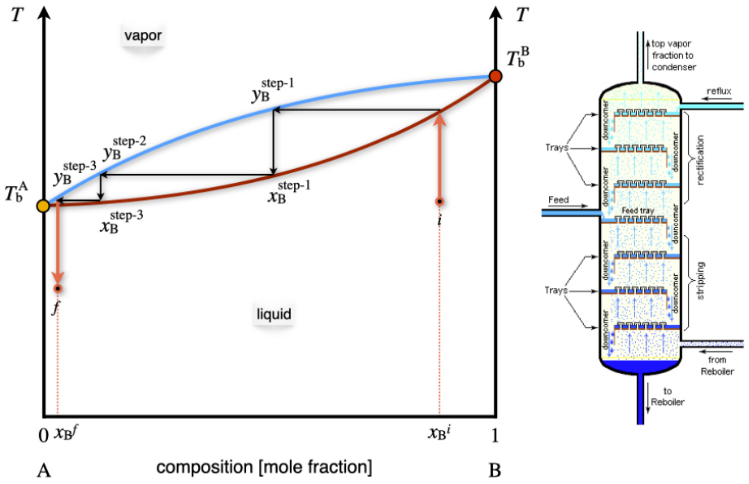


Figure 6.10.5: The Fractional Distillation Process and Theoretical Plates Calculated on a Temperature–Composition Phase Diagram.

Each of the horizontal lines in the lens region of the Tx_{B} diagram of Figure $6.10.5$ corresponds to a condensation/evaporation process and is called a *theoretical plate*. These plates are industrially realized on large columns with several floors equipped with condensation trays. The temperature decreases with the height of the column. A condensation/evaporation process will happen on each level, and a solution concentrated in the most volatile component is collected. The theoretical plates and the Tx_{B} are crucial for sizing the industrial fractional distillation columns.

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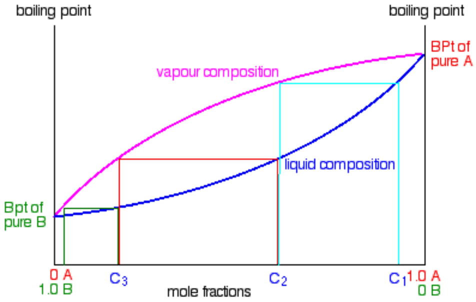
1. Only two degrees of freedom are visible in the Px_{B} diagram. Temperature represents the third independent variable.

6.11: Fractional Distillation of Ideal Mixtures

This page explains how the fractional distillation (both in the lab and industrially) of an ideal mixture of liquids relates to their phase diagram.

Using the phase diagram

On the last page, we looked at how the phase diagram for an ideal mixture of two liquids was built up. I want to start by looking again at material from the last part of that page. The next diagram is new - a modified version of diagrams from the previous page.

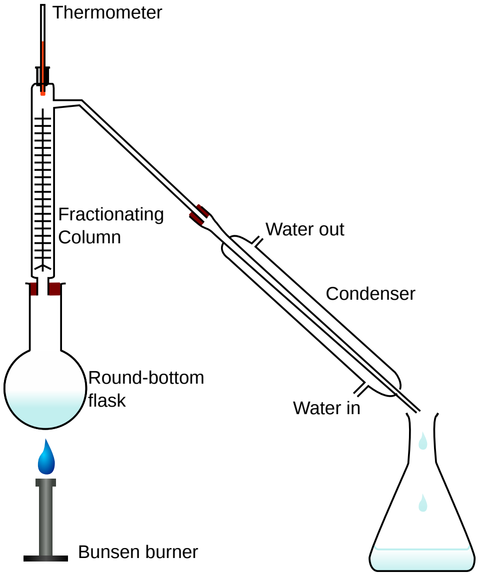


- If you boil a liquid mixture C_1, you will get a vapor with composition C_2, which you can condense to give a liquid of that same composition (the pale blue lines).
- If you reboil that liquid C_2, it will give a vapor with composition C_3. Again you can condense that to give a liquid of the same new composition (the red lines).
- Reboiling the liquid C_3 will give a vapor still richer in the more volatile component B (the green lines). You can see that if you were to do this once or twice more, you would be able to collect a liquid which was virtually pure B.

The secret of getting the more volatile component from a mixture of liquids is obviously to do a succession of boiling-condensing-reboiling operations. It is not quite so obvious how you get a sample of pure A out of this.

Fractional Distillation in the lab

A typical lab fractional distillation would look like this:

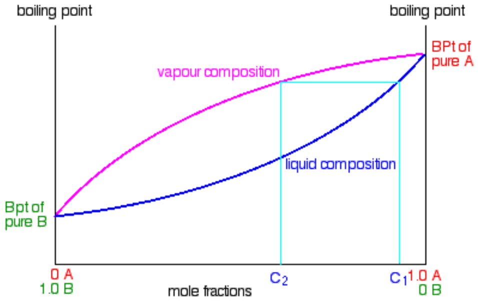


Fractional distillation setup. An Erlenmeyer flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece. (CC BY-SA 3.0; Theresa knott via Wikipedia)

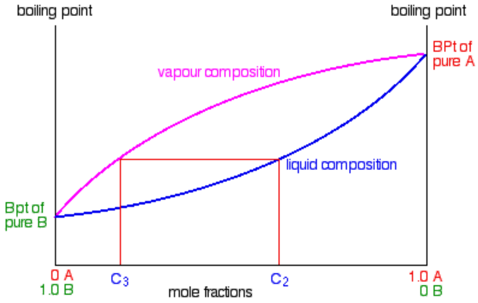
The fractionating column is packed with glass beads (or something similar) to give the maximum possible surface area for vapor to condense on. Some fractionating columns have spikes of glass sticking out from the sides which serve the same purpose. If you sketch this, make sure that you do not completely seal the apparatus. There has to be a vent in the system otherwise the pressure build-up when you heat it will blow the apparatus apart. In some cases, where you are collecting a liquid with a very low boiling point, you may need to surround the collecting flask with a beaker of cold water or ice. The mixture is heated at such a rate that the thermometer is at the temperature of the boiling point of the more volatile component. Notice that the thermometer bulb is placed exactly at the outlet from the fractionating column.

Relating what happens in the fractionating column to the phase diagram

Suppose you boil a mixture with composition C_1. The vapor over the top of the boiling liquid will be richer in the more volatile component, and will have the composition C_2.



That vapor now starts to travel up the fractionating column. Eventually it will reach a height in the column where the temperature is low enough that it will condense to give a liquid. The composition of that liquid will, of course, still be C_2. So what happens to that liquid now? It will start to trickle down the column where it will meet new hot vapor rising. That will cause the already condensed vapor to reboil.



Some of the liquid of composition C_2 will boil to give a vapor of composition C_3. Let's concentrate first on that new vapor and think about the unvaporized part of the liquid afterwards.

The vapor

This new vapor will again move further up the fractionating column until it gets to a temperature where it can condense. Then the whole process repeats itself. Each time the vapor condenses to a liquid, this liquid will start to trickle back down the column where it will be reboiled by up-coming hot vapor. Each time this happens the new vapor will be richer in the more volatile component. The aim is to balance the temperature of the column so that by the time vapor reaches the top after huge numbers of condensing and reboiling operations, it consists only of the more volatile component - in this case, B.

Whether or not this is possible depends on the difference between the boiling points of the two liquids. The closer they are together, the longer the column has to be.

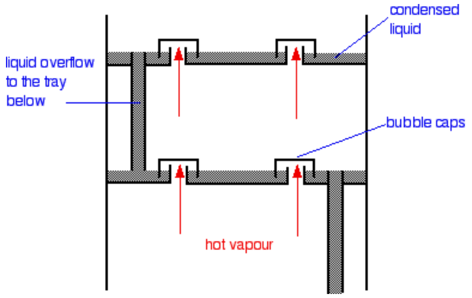
The liquid

So what about the liquid left behind at each reboiling? Obviously, if the vapor is richer in the more volatile component, the liquid left behind must be getting richer in the other one. As the condensed liquid trickles down the column constantly being reboiled by up-coming vapor, each reboiling makes it richer and richer in the less volatile component - in this case, A. By the time the liquid drips back into the flask, it will be very rich in A indeed. So, over time, as B passes out of the top of the column into the condenser, the liquid in the flask will become richer in A. If you are very, very careful over temperature control, eventually you will have separated the mixture into B in the collecting flask and A in the original flask. Finally, what is the point of the packing in the column?

To make the boiling-condensing-reboiling process as effective as possible, it has to happen over and over again. By having a lot of surface area inside the column, you aim to have the maximum possible contact between the liquid trickling down and the hot vapor rising. If you didn't have the packing, the liquid would all be on the sides of the condenser, while most of the vapor would be going up the middle and never come into contact with it.

Fractional distillation industrially

There is no difference whatsoever in the theory involved. All that is different is what the fractionating column looks like. The diagram shows a simplified cross-section through a small part of a typical column.

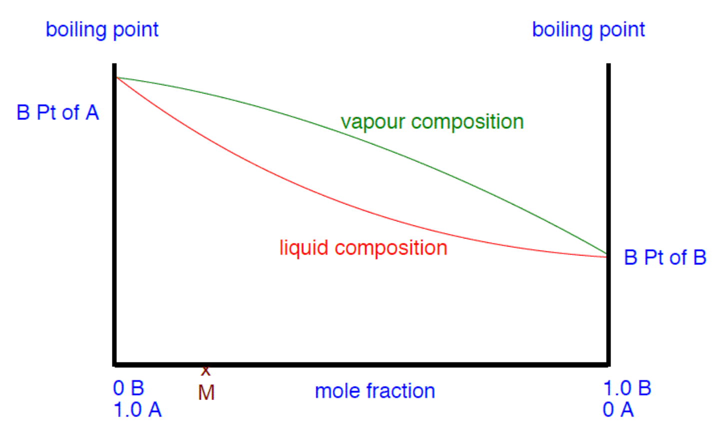


The column contains a number of trays that the liquid collects on as the vapor condenses. The up-coming hot vapor is forced through the liquid on the trays by passing through a number of bubble caps. This produces the maximum possible contact between the vapor and liquid. This all makes the boiling-condensing-reboiling process as efficient as possible. The overflow pipes are simply a controlled way of letting liquid trickle down the column.

If you have a mixture of lots of liquids to separate (such as in petroleum fractionation), it is possible to tap off the liquids from some of the trays rather than just collecting what comes out of the top of the column. That leads to simpler mixtures such as gasoline, kerosene and so on.

✓ Example 1

a. Use the phase diagram below to explain how you can obtain a pure sample of B from a mixture M by successively boiling and condensing the liquid mixture.



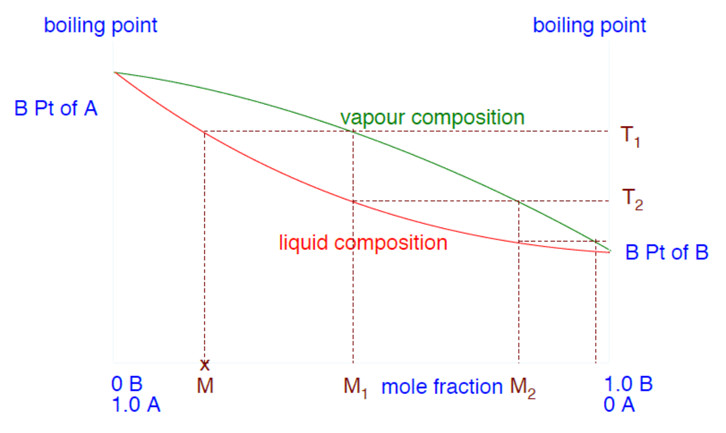
b. Why is it important to carefully control how strongly the original mixture is heated during the separation?
c. Explain briefly how the separation occurs, making use of the phase diagram above if you think it helps.

Solution

a. If you boil the mixture M, it will boil at a temperature T1. The vapor above the liquid at this temperature will be richer in the more volatile substance B. If you condense that vapor, it will give a liquid of the composition M1. If you reboil that, it will boil at a temperature T2. The vapor over that liquid will have a composition M2, still richer in B. If you go on doing that, reboiling and recondensing, then the vapor becomes richer and richer in B until it eventually becomes pure B. When you finally get to that point and condense the vapor, then you will have pure B liquid.

b. You have to be sure that only the vapor of the more volatile of the two liquids passes into the condenser. That means that the thermometer has to read exactly the boiling point of the more volatile liquid. If it is below that, then nothing is going to pass out into the condenser. If it is above that, then your distillate will still contain some of the less volatile component.

c. B is the more volatile liquid; A is the less volatile one. The vapor over the boiling liquid in the flask will be richer in B than the original liquid is. That vapor will pass up the column until the temperature falls enough for it to condense to give a liquid richer in B than the one in the flask (equivalent to M1 in the diagram). This will start to trickle down the column. Hot vapor coming up from the flask will reboil the condensed liquid, giving a vapor which will be even richer in B (M2 on the diagram). This will condense to a liquid, trickle down the column and then be reboiled. This continuous process will go on until the vapor is entirely B. The column is heated so that this is finally complete right at the top of the column. Meanwhile, the liquids trickling down the column get richer and richer in A as the B is removed and carried up the column. Eventually, the liquid in the flask will end up as pure A.



6.12: Most Solutions are Not Ideal

If we plot the partial pressure of one component, P_1, above a mixture with a mole fraction x_1, we should get a straight line with a slope of P_1^* (Raoult's law). Above non-ideal solutions the graph will no longer be a straight line but a curve. However towards $x_1 = 1$ the curve typically approaches the Raoult line. On the other extreme, there often is a more or less linear region as well, ***but with a different slope*** (Figure 24.5.1). This means that we can identify two *limiting* laws:

- For $x \rightarrow 0$: **Henry's law**:

$$P_1 = K_H x_1$$

- For $x \rightarrow 1$: **Raoult's law**:

$$P_1 = P_1^* x_1$$

This implies that the straight line that indicates the Henry expression will intersect the y-axis at $x = 1$ (pure compound) at a ***different*** point than P^*. For $x \rightarrow 0$ (low concentrations) we can speak of component 1 being the *solute* (the minority component). At the other end $x \rightarrow 1$ it plays the role of the *solvent* (majority component).

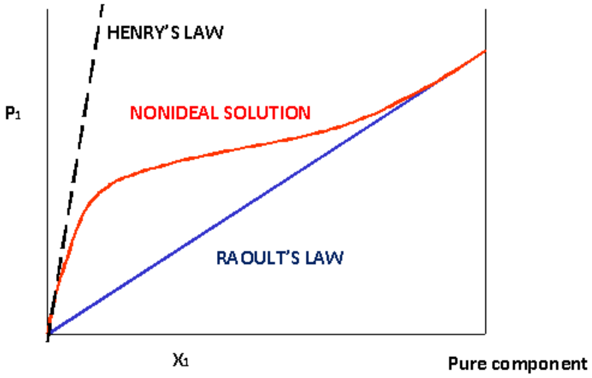


Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> Another thing to note is that P^* is a property of *one pure component*, the value of K_H by contrast is a property of the *combination of two components*, so it needs to be measured for each solute-solvent combination.

As you can see we have a description for both the high and the low end, but not in the middle. In general, the more modest the deviations from ideality the larger the range of validity of the two limiting laws. The way to determine K_H would be to actually determine vapor pressures. How about the other component? Do we need to measure them too? Fortunately we can use thermodynamics to answer this question with no. There is a handy expression that saves us the trouble.

6.13: Phase Diagrams of Non-Ideal Solutions

Non-ideal solutions follow Raoult's law for only a small amount of concentrations. The typical behavior of a non-ideal solution with a single volatile component is reported in the Px_{B} plot in Figure $6.13.1$.

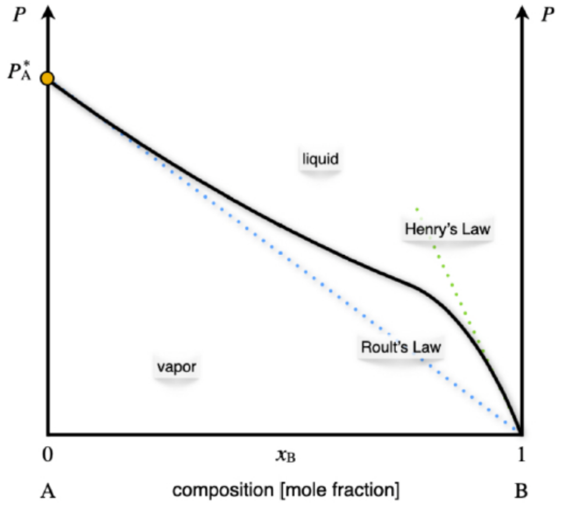


Figure 6.13.1: The Pressure–Composition Phase Diagram of a Non-Ideal Solution Containing a Single Volatile Component at Constant Temperature.

Raoult's behavior is observed for high concentrations of the volatile component. This behavior is observed at $x_{\text{B}} \to 0$ in Figure $6.13.1$, since the volatile component in this diagram is A. At low concentrations of the volatile component $x_{\text{B}} \to 1$ in Figure $6.13.1$, the solution follows a behavior along a steeper line, which is known as **Henry's law**. William Henry (1774–1836) has extensively studied the behavior of gases dissolved in liquids. His studies resulted in a simple law that relates the vapor pressure of a solution to a constant, called Henry's law solubility constants:

$$P_{\text{B}} = k_{\text{AB}} x_{\text{B}}, \tag{6.13.1}$$

where k_{AB} depends on the chemical nature of A and B. The corresponding diagram for non-ideal solutions with two volatile components is reported on the left panel of Figure $6.13.2$. The total pressure is once again calculated as the sum of the two partial pressures. Positive deviations on Raoult's ideal behavior are not the only possible deviation from ideality, and negative deviation also exits, albeit slightly less common. An example of a negative deviation is reported in the right panel of Figure $6.13.2$.

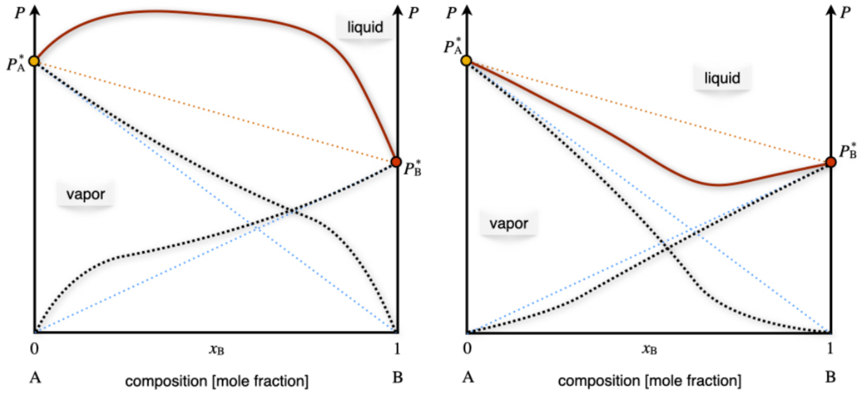


Figure 6.13.2: The Pressure–Composition Phase Diagram of Non-Ideal Solutions Containing Two Volatile Components at Constant Temperature.

If we move from the Px_{B} diagram to the Tx_{B} diagram, the behaviors observed in Figure $6.13.2$ will correspond to the diagram in Figure $6.13.3$.

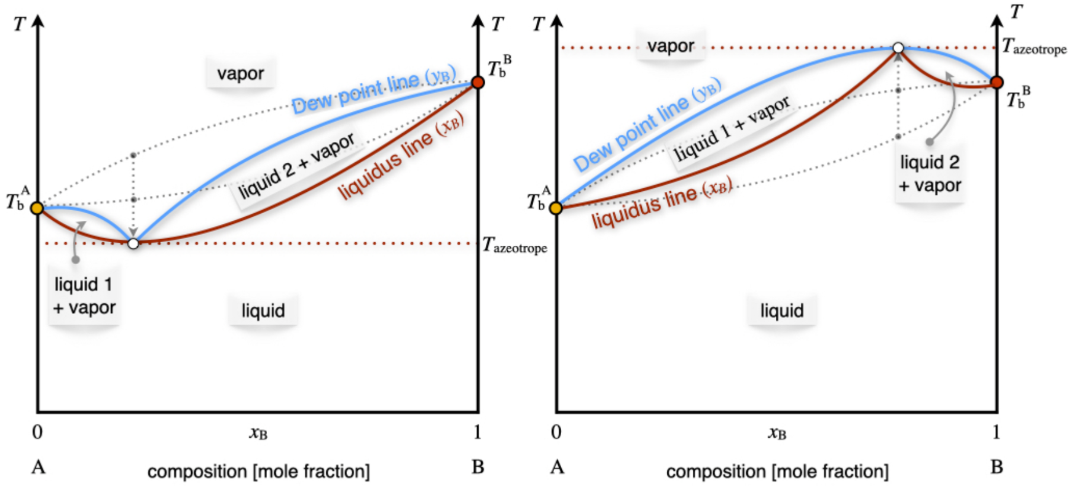


Figure $6.13.3$: The Temperature–Composition Phase Diagram of Non-Ideal Solutions Containing Two Volatile Components at Constant Pressure.

The minimum (left plot) and maximum (right plot) points in Figure $6.13.3$ represent the so-called **azeotrope**.

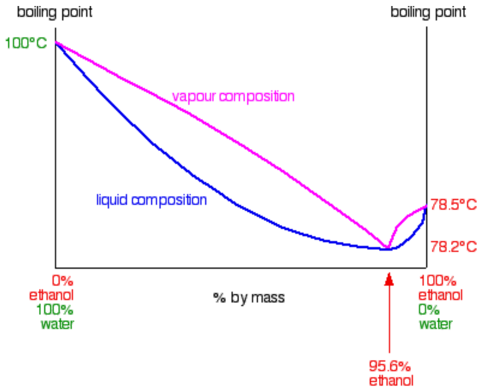
An azeotrope is a constant boiling point solution whose composition cannot be altered or changed by simple distillation. This happens because the liquidus and Dew point lines coincide at this point. Therefore, the liquid and the vapor phases have the same composition, and distillation cannot occur. Two types of azeotropes exist, representative of the two types of non-ideal behavior of solutions. The first type is the positive azeotrope (left plot in Figure $6.13.3$). A notorious example of this behavior at atmospheric pressure is the ethanol/water mixture, with composition 95.63% ethanol by mass. This positive azeotrope boils at $T = 78.2\ ^\circ\text{C}$, a temperature that is lower than the boiling points of the pure constituents, since ethanol boils at $T = 78.4\ ^\circ\text{C}$ and water at $T = 100\ ^\circ\text{C}$. The second type is the negative azeotrope (right plot in Figure $6.13.3$). An example of this behavior at atmospheric pressure is the hydrochloric acid/water mixture with composition 20.2% hydrochloric acid by mass. This negative azeotrope boils at $T = 110\ ^\circ\text{C}$, a temperature that is higher than the boiling points of the pure constituents, since hydrochloric acid boils at $T = -84\ ^\circ\text{C}$ and water at $T = 100\ ^\circ\text{C}$.

6.14: Fractional Distillation of Non-ideal Mixtures (Azeotropes)

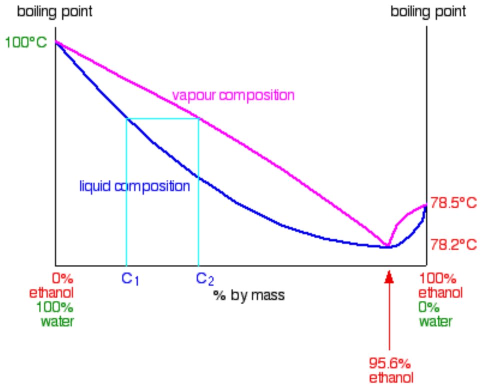
Positive Deviation from Raoult's Law

Remember that a large positive deviation from Raoult's Law produces a vapor pressure curve with a maximum value at some composition other than pure A or B. If a mixture has a high vapor pressure it means that it will have a low boiling point. The molecules are escaping easily and you won't have to heat the mixture much to overcome the intermolecular attractions completely. The implication of this is that the boiling point / composition curve will have a minimum value lower than the boiling points of either A or B.

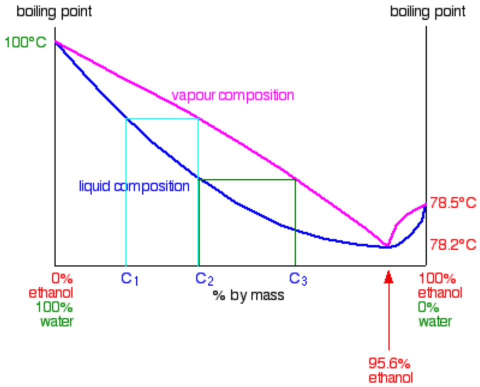
In the case of mixtures of ethanol and water, this minimum occurs with 95.6% by mass of ethanol in the mixture. The boiling point of this mixture is 78.2°C, compared with the boiling point of pure ethanol at 78.5°C, and water at 100°C. You might think that this 0.3°C doesn't matter much, but it has huge implications for the separation of ethanol / water mixtures. The next diagram shows the boiling point / composition curve for ethanol / water mixtures. I've also included on the same diagram a vapor composition curve in exactly the same way as we looked at on the previous pages about phase diagrams for ideal mixtures.



Suppose you are going to distil a mixture of ethanol and water with composition C_1 as shown on the next diagram. It will boil at a temperature given by the liquid curve and produce a vapor with composition C_2.



When that vapor condenses it will, of course, still have the composition C_2. If you reboil that, it will produce a new vapor with composition C_3.



You can see that if you carried on with this boiling-condensing-reboiling sequence, you would eventually end up with a vapor with a composition of 95.6% ethanol. If you condense that you obviously get a liquid with 95.6% ethanol.

What happens if you reboil that liquid? The liquid curve and the vapor curve meet at that point. The vapor produced will have that same composition of 95.6% ethanol. If you condense it again, it will still have that same composition. You have hit a barrier. It is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% of ethanol. This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapor composition is exactly the same as the liquid. It is known as a constant boiling mixture or **an azeotropic mixture** or an **azeotrope**.

The implications of this for fractional distillation of dilute solutions of ethanol are obvious. The liquid collected by condensing the vapor from the top of the fractionating column cannot be pure ethanol. The best you can produce by simple fractional distillation is 95.6% ethanol. What you can get (although it isn't very useful!) from the mixture is pure water. As ethanol rich vapor is given off from the liquid boiling in the distillation flask, it will eventually lose all the ethanol to leave just water.

To Summarize

Distilling a mixture of ethanol containing less than 95.6% of ethanol by mass lets you collect:

- a distillate containing 95.6% of ethanol in the collecting flask (provided you are careful with the temperature control, and the fractionating column is long enough);
- pure water in the boiling flask.

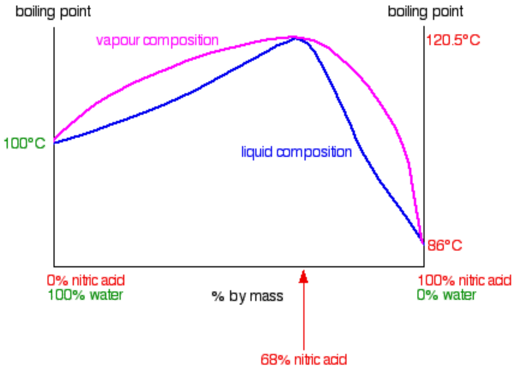
What if you distil a mixture containing more than 95.6% ethanol? Work it out for yourself using the phase diagram, and starting with a composition to the right of the azeotropic mixture. You should find that you get:

- a distillate containing 95.6% of ethanol in the collecting flask (provided you are careful with the temperature control and the fractionating column is long enough);
- pure ethanol in the boiling flask.

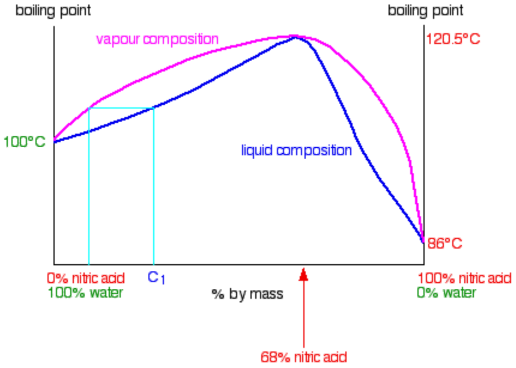
A negative deviation from Raoult's Law

Nitric acid and water form mixtures in which particles break away to form the vapor with much more difficulty than in either of the pure liquids. You can see this from the vapor pressure / composition curve discussed further up the page. That means that mixtures of nitric acid and water can have boiling points higher than either of the pure liquids because it needs extra heat to break the stronger attractions in the mixture.

In the case of mixtures of nitric acid and water, there is a maximum boiling point of 120.5°C when the mixture contains 68% by mass of nitric acid. That compares with the boiling point of pure nitric acid at 86°C, and water at 100°C. Notice the much bigger difference this time due to the presence of the new ionic interactions (see above). The phase diagram looks like this:



Distilling dilute nitric acid. Start with a dilute solution of nitric acid with a composition of C_1 and trace through what happens.

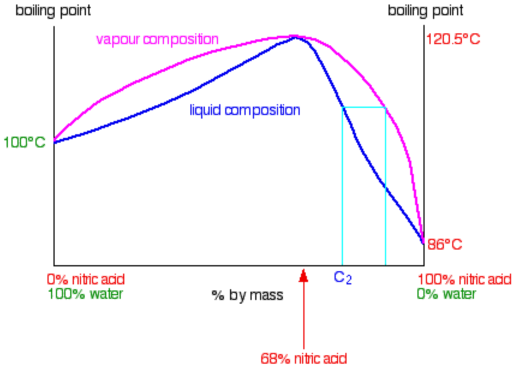


The vapor produced is richer in water than the original acid. If you condense the vapor and reboil it, the new vapor is even richer in water. Fractional distillation of dilute nitric acid will enable you to collect pure water from the top of the fractionating column. As the acid loses water, it becomes more concentrated. Its concentration gradually increases until it gets to 68% by mass of nitric acid. At that point, the vapor produced has exactly the same concentration as the liquid, because the two curves meet. You produce a constant boiling mixture (or azeotropic mixture or azeotrope) and if you distil dilute nitric acid, that's what you will eventually be left with in the distillation flask. You cannot produce pure nitric acid from the dilute acid by distilling it.

> *You cannot produce pure nitric acid from the dilute acid (<68%) by distilling it.*

Distilling nitric acid more concentrated than 68% by mass

This time you are starting with a concentration C_2 to the right of the azeotropic mixture.



The vapor formed is richer in nitric acid. If you condense and reboil this, you will get a still richer vapor. If you continue to do this all the way up the fractionating column, you can get pure nitric acid out of the top. As far as the liquid in the distillation flask is concerned, it is gradually losing nitric acid. Its concentration drifts down towards the azeotropic composition. Once it reaches that, there cannot be any further change, because it then boils to give a vapor with the same composition as the liquid. Distilling a nitric acid / water mixture containing more than 68% by mass of nitric acid gives you pure nitric acid from the top of the fractionating column and the azeotropic mixture left in the distillation flask.

> *You can produce pure nitric acid from the concetrated acid (>68%) by distilling it.*

Contributors and Attributions

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6.15: Activity

For non-ideal gases, we introduced in chapter 11 the concept of *fugacity* as an *effective pressure* that accounts for non-ideal behavior. If we extend this concept to non-ideal solution, we can introduce the *activity* of a liquid or a solid, a, as:

$$\mu_{\text{non-ideal}} = \mu^{-\ominus} + RT \ln a, \tag{6.15.1}$$

where μ is the chemical potential of the substance or the mixture, and $\mu^{-\ominus}$ is the chemical potential at standard state. Comparing this definition to Equation 11.4.2, it is clear that the activity is equal to the fugacity for a non-ideal gas (which, in turn, is equal to the pressure for an ideal gas). However, for a liquid and a liquid mixture, it depends on the chemical potential at standard state. This means that the activity is not an absolute quantity, but rather a relative term describing how "active" a compound is compared to standard state conditions. The choice of the standard state is, in principle, arbitrary, but conventions are often chosen out of mathematical or experimental convenience. We already discussed the convention that standard state for a gas is at $P^{-\ominus} = 1$ bar, so the activity is equal to the fugacity. The standard state for a component in a solution is the pure component at the temperature and pressure of the solution. This definition is equivalent to setting the activity of a pure component, i, at $a_i = 1$.

For a component in a solution we can use Equation 11.4.2 to write the chemical potential in the gas phase as:

$$\mu_i^{\text{vapor}} = \mu_i^{-\ominus} + RT \ln \frac{P_i}{P^{-\ominus}}. \tag{6.15.2}$$

If the gas phase is in equilibrium with the liquid solution, then:

$$\mu_i^{\text{solution}} = \mu_i^{\text{vapor}} = \mu_i^*, \tag{6.15.3}$$

where μ_i^* is the chemical potential of the pure element. Subtracting Equation 6.15.3 from Equation 6.15.2, we obtain:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}. \tag{6.15.4}$$

For an ideal solution, we can use Raoult's law, Equation 13.1.1, to rewrite Equation 6.15.4 as:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i, \tag{6.15.5}$$

which relates the chemical potential of a component in an ideal solution to the chemical potential of the pure liquid and its mole fraction in the solution. For a non-ideal solution, the partial pressure in Equation 6.15.4 is either larger (positive deviation) or smaller (negative deviation) than the pressure calculated using Raoult's law. The chemical potential of a component in the mixture is then calculated using:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln(\gamma_i x_i), \tag{6.15.6}$$

where γ_i is a positive coefficient that accounts for deviations from ideality. This coefficient is either larger than one (for positive deviations), or smaller than one (for negative deviations). The activity of component i can be calculated as an *effective mole fraction*, using:

$$a_i = \gamma_i x_i, \tag{6.15.7}$$

where γ_i is defined as the **activity coefficient**. The partial pressure of the component can then be related to its vapor pressure, using:

$$P_i = a_i P_i^*. \tag{6.15.8}$$

Comparing Equation 6.15.8 with Raoult's law, we can calculate the activity coefficient as:

$$\gamma_i = \frac{P_i}{x_i P_i^*} = \frac{P_i}{P_i^{\text{R}}}, \tag{6.15.9}$$

where P_i^{R} is the partial pressure calculated using Raoult's law. This result also proves that for an ideal solution, $\gamma = 1$. Equation 6.15.9 can also be used experimentally to obtain the activity coefficient from the phase diagram of the non-ideal solution. This is achieved by measuring the value of the partial pressure of the vapor of a non-ideal solution. Examples of this procedure are reported for both positive and negative deviations in Figure 6.15.1.

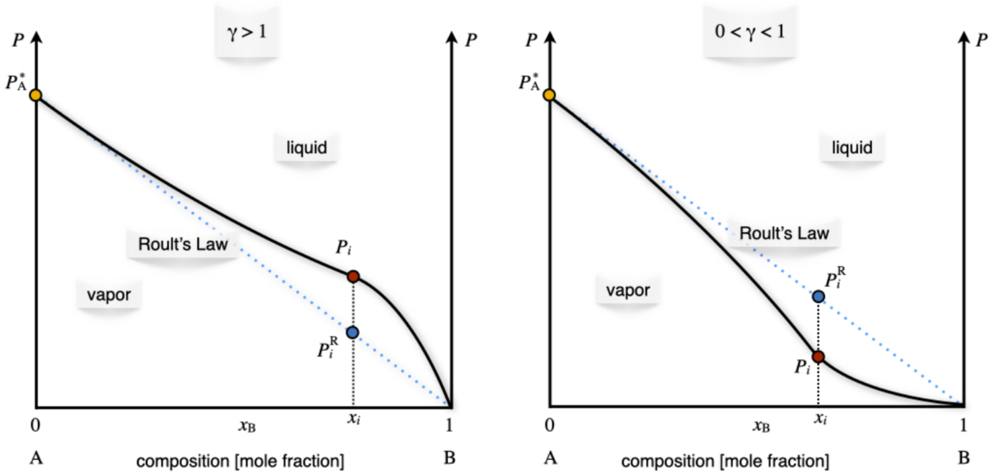


Figure 6.15.1: Positive and Negative Deviation from Raoult's Law in the Pressure–Composition Phase Diagram of Non-Ideal Solutions at Constant Temperature.

- As we already discussed in chapter 10, the activity is the most general quantity that we can use to define the equilibrium constant of a reaction (or the reaction quotient). The advantage of using the activity is that it's defined for ideal and non-ideal gases and mixtures of gases, as well as for ideal and non-ideal solutions in both the liquid and the solid phase.[1]

---

[1] Notice that, since the activity is a relative measure, the equilibrium constant expressed in terms of the activities is also a relative concept. In other words, it measures equilibrium relative to a standard state. This fact, however, should not surprise us, since the equilibrium constant is also related to $\Delta_{\text{rxn}}G^{-\ominus}$ using Gibbs' relation. This is why the definition of a universally agreed-upon standard state is such an essential concept in chemistry, and why it is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe.

CHAPTER OVERVIEW

7: Chemical Equilibrium

7.1: Equilibrium Results when Gibbs Energy is Minimized

Many important chemical reactions -if not *most*- are performed in *solution* rather than between solids or gases. Solid state reactions are often very slow and not all chemical species can be put in the vapor phase because they decompose before evaporating.

Often we are not concerned with the temporal aspects of a reaction. That can be technologically very important but it is the domain of *kinetics* - a different branch of Physical Chemistry - rather than classical thermodynamics.. The latter is more concerned with the endpoint. This is the thermodynamically speaking the (stable) equilibrium, but chemically it can either represent a *completed* reaction or a *chemical equilibrium*.

Unfortunately, of the three main aggregation states: gas – liquid – solid, the structure of liquids is least understood and one of the most complex liquids is also one of the most extensively used ones: water. It is vital to many branches of chemistry varying from geochemistry to environmental chemistry to biochemistry. We shall make just a small inroad into its complexity.

7.1.1: Extent of reaction

To describe the progress of a reaction we define the **extent of reaction**. It is usually denoted by the Greek letter ξ.

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

Using stoichiometry we can define the extent by considering how the number of moles (or molar amounts) of each species changes during the reaction:

reactants

- $n_A = n_{A,0} - v_A \xi$
- $n_B = n_{B,0} - v_B \xi$

products

- $n_Y = n_{Y,0} + v_Y \xi$
- $n_Z = n_{Z,0} + v_Z \xi$

The dimension of ξ is [mol] because the stoichiometric coefficients v_i are dimensionless integers. If the reaction goes to completion for one of the reactants -the *limiting reactant*- $n_{A \text{ or } B}$=n_{limiting} will go to zero. If we start with $n_{limiting} = v_{limiting}$ moles, the value of ξ starts at 0 (no products) and goes to 1 at completion (limiting reactant depleted). When approaching an equilibrium ξ will not go beyond ξ_{eq}.

7.1.2: Measuring ξ

The extent of reaction is what is the central subject of reaction kinetics. Its value is typically measured as a function of time indirectly by measuring a quantity q that is *linearly dependent* on ξ(t):

$$q(\xi) = a\xi + b$$

Consider the situation at the extremes $\xi = 0$ and $\xi = 1$:

$$q_0 = a.0 + b = b$$

$$q_1 = a.1 + b = a + b$$

$$q_1 - q_0 = a$$

Thus, ξ can be found from

$$\frac{q(t) - q0}{q_1 - q_0} = \frac{q(t) - b}{a}$$

The nature of q can vary widely from UV/Vis absorption, conductivity, gravimetric to caloric data.

In practice, q_0 at $\xi = 0$ is often hard to observe because it takes time to mix the reactants, particularly in solutions, and q_1 at ξ=1 may never be reached if the reaction goes to equilibrium. Nevertheless the values of a and b can often be found from the available data by fitting techniques.

In (equilibrium, static) thermodynamics we are only concerned with the endpoint:

- $\xi = 1$: the reaction runs to completion
- $\xi = \xi_{eq}$: the react ion goes to a state of chemical equilibrium

7.1.3: Thermodynamic Potentials

As we have seen we can write any change in the Gibbs free energy due to changes in the molar amounts of the species involved in the reaction (at T, P constant) as:

$$dG = \sum \frac{\partial G}{\partial n_i} dn_i = \sum \mu_i dn_i$$

where μ is the *thermodynamic potential*, often called *chemical potential* when dealing with reactions. From the definition of ξ we can see by differentiation that

- $dn_A = -v_A d\xi$
- $dn_B = -v_A d\xi$
- $dn_Y = v_Y d\xi$
- $dn_Z = v_Z d\xi$

This allows us to *unify the changes* in the molar amount of all the species into *one single variable* $d\xi$. We get:

$$dG = \left[\sum -v_{i,reactants}\,\mu_{i,reactants} + \sum +v_{i,products}\,\mu_{j,products}\right] d\xi$$

or

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\sum v_{i,r}\mu_{i,r} + \sum v_{i,p}\mu_{j,p}$$

This quantity is also written as:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G$$

This quantity gives the change in Gibbs free energy for the reaction (as written!!) for Δξ=1 mole. (Units are [J/mol] therefore). This is the change in Gibbs energy (the slope of G vs ξ) when the extent of reaction changes by one mole with a fixed composition. Equilibrium results when Gibbs energy is at a minimum with respect to the extent of reaction.

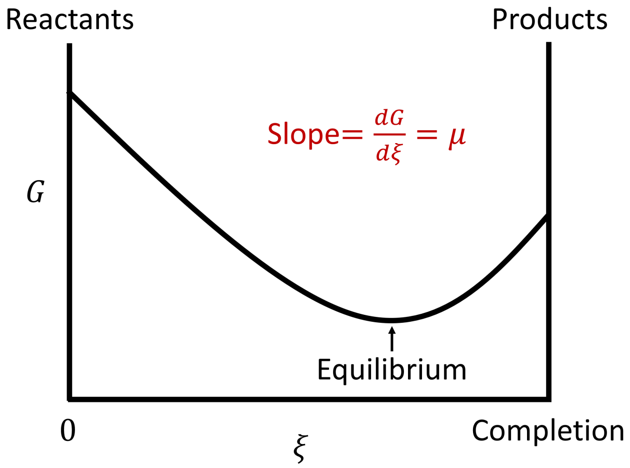


Figure 1. Gibbs energy plotted as a function of the extent of reaction. Equilibrium results when the Gibbs energy is minimized.

7.1.4: Gas Reactions

Let us assume that our reaction is entirely between gas species and that the gas is sufficiently dilute that we can use the ideal gas law. Then we can write for each species:

$$\mu_i = \mu_i^o + RT \ln \frac{P_i}{P_i^o}$$

We can then split up the $\Delta_r G$ expression in two parts:

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

The standard potentials:

$$\Delta_r G^o = -\sum v_{i,r}\, \mu_{i,r}^o + \sum v_{i,p} \mu_{j,p}^o$$

and the logarithmic terms:

$$RT \ln Q = -v_A RT \ln\left(\frac{P_A}{P_A^o}\right) - v_B RT \ln\left(\frac{P_B}{P_B^o}\right) + v_Y RT \ln\left(\frac{P_Y}{P_Y^o}\right) + v_Z RT \ln\left(\frac{P_Z}{P_Z^o}\right)$$

We can combine all the logarithmic terms into Q, called the ***reaction quotient***. The stoichiometric coefficients become exponents and the reactants' factors will be 'upside down' compared to the products, because of the properties of logarithms:

$$a \ln x = \ln x^a$$

$$-a \ln x = \ln\left(\frac{1}{x^a}\right)$$

We have kept the standard pressures P_i^o in the expression, but often they are omitted. They are usually all 1 bar, but in principle we could choose 1 bar for A 1 Torr for B an 1 psi for the products. It creates a valid (though ridiculous) definition of what ⦵ stands for. (Of course the value of $\Delta_r G^o$ does *depend* on that choice!).

We could write

$$RT \ln Q = RT \ln \frac{Q_P}{Q^o}$$

Q^o is typically unity in magnitude but it *cancels the dimensions* of Q_P. That means that Q and Q_P are equal in magnitude and we can get Q from Q_P by simply dropping the dimensions. Q is dimensionless but Q_P usually is not. Often this fine distinction is simply not made and Q^o is *omitted*, we get:

$$\Delta_r G = \Delta_r G^o + RT \ln \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}}$$

Notice the difference between $\Delta_r G$ which denotes the conditions (e.g. pressures) of *your reaction* and $\Delta_r G^o$ denotes standard conditions.

7.2: Reaction Quotient and Equilibrium Constant

Let’s consider a prototypical reaction at constant T, P:

$$a\mathrm{A}+b\mathrm{B}\rightarrow c\mathrm{C}+d\mathrm{D} \tag{7.2.1}$$

The Gibbs free energy of the reaction is defined as:

$$\Delta_{\mathrm{rxn}}G=G_{\mathrm{products}}-G_{\mathrm{reactants}}=G^{\mathrm{C}}+G^{\mathrm{D}}-G^{\mathrm{A}}-G^{\mathrm{B}}, \tag{7.2.2}$$

and replacing the absolute Gibbs free energies with the chemical potentials μ_i, we obtain:

$$\Delta_{\mathrm{rxn}}G=c\mu_{\mathrm{C}}+d\mu_{\mathrm{D}}-a\mu_{\mathrm{A}}-b\mu_{\mathrm{B}}. \tag{7.2.3}$$

Assuming the reaction is happening in the gas phase, we can then use Equation 9.4.6 to replace the chemical potentials with their value in the reaction mixture, as:

$$\begin{aligned}\Delta_{\mathrm{rxn}}G= &\ c(\mu_{\mathrm{C}}^{\ominus}+RT\ln P_{\mathrm{C}})+d(\mu_{\mathrm{D}}^{\ominus}+RT\ln P_{\mathrm{D}})-a(\mu_{\mathrm{A}}^{\ominus}+RT\ln P_{\mathrm{A}})-b(\mu_{\mathrm{B}}^{\ominus}+RT\ln P_{\mathrm{B}})\\ = &\ \underbrace{c\mu_{\mathrm{C}}^{\ominus}+d\mu_{\mathrm{D}}^{\ominus}-a\mu_{\mathrm{A}}^{\ominus}-b\mu_{\mathrm{B}}^{\ominus}}_{\Delta_{\mathrm{rxn}}G^{\ominus}}+RT\ln\frac{P_{\mathrm{C}}^{c}\cdot P_{\mathrm{D}}^{d}}{P_{\mathrm{A}}^{a}\cdot P_{\mathrm{B}}^{b}}.\end{aligned} \tag{7.2.4}$$

We can define a new quantity called the *reaction quotient* as a function of the partial pressures of each substance:[1])

$$Q_P=\frac{P_{\mathrm{C}}^{c}\cdot P_{\mathrm{D}}^{d}}{P_{\mathrm{A}}^{a}\cdot P_{\mathrm{B}}^{b}}, \tag{7.2.5}$$

and we can then simply rewrite Equation 7.2.4 using Equation 7.2.5 as:

$$\Delta_{\mathrm{rxn}}G=\Delta_{\mathrm{rxn}}G^{\ominus}+RT\ln Q_P. \tag{7.2.6}$$

This equation tells us that the sign of $\Delta_{\mathrm{rxn}}G$ is influenced by the reaction quotient Q_P. For a spontaneous reaction at the beginning, the partial pressures of the reactants are much higher than the partial pressures of the products, therefore $Q_P\ll 1$ and $\Delta_{\mathrm{rxn}}G<0$, as we expect. As the reaction proceeds, the partial pressures of the products will increase, while the partial pressures of the reactants will decrease. Consequently, both Q_P and $\Delta_{\mathrm{rxn}}G$ will increase. The reaction will completely stop when $\Delta_{\mathrm{rxn}}G=0$, which is the chemical equilibrium point. At the reaction equilibrium:

$$\Delta_{\mathrm{rxn}}G=0=\Delta_{\mathrm{rxn}}G^{\ominus}+RT\ln K_P, \tag{7.2.7}$$

where we have defined a new quantity called **equilibrium constant**, as the value the reaction quotient assumes when the reaction reaches equilibrium, and we have denoted it with the symbol K_P.[2] From Equation 7.2.7 we can derive the following fundamental equation on the standard Gibbs free energy of reaction:

$$\Delta_{\mathrm{rxn}}G^{\ominus}=-RT\ln K_P. \tag{7.2.8}$$

To extend the concept of K_P beyond the four species in the prototypical reaction (10.1), we can use the product of a series symbol ($\prod_i$), and write:

$$K_P=\prod_i P_{i,\mathrm{eq}}^{\nu_i}, \tag{7.2.9}$$

where $P_{i,\mathrm{eq}}$ are the partial pressure of each species at equilibrium. Eq. (10.1.9) is in principle valid for ideal gases only. However, reaction involving ideal gases are pretty rare. As such, we can further extend the concept of equilibrium constant and write:

$$K_{\mathrm{eq}}=\prod_i a_{i,\mathrm{eq}}^{\nu_i}, \tag{7.2.10}$$

where we have replaced the partial pressure at equilibrium, $P_{i,\mathrm{eq}}$, with a new concept introduced initially by Gilbert Newton Lewis (1875–1946),[3] that he termed **activity**, and represented by the letter a. For ideal gases, it is clear that $a_i=P_i/P^{\ominus}$. For non-ideal gases, the activity is equal to the fugacity $a_i=f_i/P^{\ominus}$, a concept that we will investigate in the next chapter. For pure liquids and solids, the activity is simply $a_i=1$. For diluted solutions, the activity is equal to a measured concentration (such as, for example, the mole fraction x_i in the liquid phase, and y_i in the gas phase, or the molar concentration $[i]/[i]^{\ominus}$ with $[i]^{\ominus}=1\ [mol/L]$). Finally for concentrated solutions, the activity is related to the measured concentration via an activity coefficient. We will return to the concept of activity in chapter 14, when we will specifically deal with solutions. For now, it is interesting to use the activity to write the definition of the following two constants:

$$K_y = \prod_i \left(y_{i,\text{eq}}\right)^{\nu_i} \qquad\qquad K_C = \left(\prod_i [i]_{\text{eq}}/[i]^{\ominus}\right)^{\nu_i}, \tag{7.2.11}$$

which can then be related with K_P for a mixture of ideal gases using:

$$P_i = y_i P \qquad\qquad P_i = \frac{n_i}{V}RT = [i]RT, \tag{7.2.12}$$

which then results in:

$$K_P = K_y \cdot \left(\frac{P}{P^{\ominus}}\right)^{\Delta\nu} \qquad\qquad K_P = K_C \left(\frac{[i]^{\ominus}RT}{P^{\ominus}}\right)^{\Delta\nu}, \tag{7.2.13}$$

with $\Delta\nu = \sum_i \nu_i$.

Using the general equilibrium constant, K_{eq}, we can also rewrite the fundamental equation on $\Delta_{\text{rxn}}G^{\ominus}$ that we derived in Equation 7.2.8 to be applicable at most conditions, as:

$$\Delta_{\text{rxn}}G^{\ominus} = -RT\ln K_{\text{eq}}, \tag{7.2.14}$$

and since $\Delta_{\text{rxn}}G^{\ominus}$ depends on T, P and $\{n_i\}$, it is useful to explore how K_{eq} depends on those variables as well.

---

1. Notice that since we used Equation 9.4.5 to derive the reaction quotient, the partial pressures inside it are always dimensionless since they are divided by $P^{\ominus}$.
2. The subscript P refers to the fact that the equilibrium constant is measured in terms of partial pressures.
3. Gilber Lewis is the same scientist that invented the concept of Lewis Structures.

7.3: An Equilibrium Constant is a Function of Temperature Only

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

When the reaction reaches equilibrium, the Gibbs energy of reaction, $\Delta_r G$, goes to zero. In this case, the reaction quotient, Q, is usually rewritten as the **equilibrium constant**, K, and we get:

$$\Delta_r G = \Delta_r G^o + RT \ln K = 0$$

$$\Delta_r G^o = -RT \ln K$$

where

$$K = \frac{P_{eq,Y}^{vY} P_{eq,Z}^{vZ}}{P_{eq,A}^{vA} P_{eq,B}^{vB}}$$

Note

As you see $\Delta_r G^o$ is ***not*** zero, because the standard state does ***not*** represent an equilibrium state (typically).

We can calculate the temperature dependence of K. Rather than look at:

$$\left(\frac{\partial K}{\partial T}\right)_P$$

We will look at:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P$$

Starting with Gibbs energy:

$$\Delta_r G^\circ = -RT \ln K$$

$$\therefore \ln K = -\frac{\Delta r G^\circ}{RT}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{1}{R}\left[\frac{\partial(\Delta_r G^\circ/T)}{\partial T}\right]_P$$

We need to take the Gibbs-Helmholtz equation:

$$\Delta \bar{H} = -T^2\left[\frac{\partial(\Delta \bar{G}/T)}{\partial T}\right]_P$$

We can also write it as:

$$\left[\frac{\partial\left(\Delta \bar{G}/T\right)}{\partial T}\right]_P = -\frac{\Delta \bar{H}}{T^2}$$

Plugging the Gibbs-Helmholtz equation into our earlier equation, we obtain the Van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2}$$

The temperature dependence of the equilibrium constant depends on enthalpy of reaction. Rearranging:

$$d\left(\ln K\right) = \frac{\Delta_r H^\circ(T)}{RT^2} dT$$

This is the Van't Hoff equation. We can use it to find K at other temperatures. Assuming enthalpy is independent of temperature, the integrated form becomes:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

7.3.1: Le Chatelier's Principle

In the ideal gas reaction case, K **only** depends on temperature, T, (just like U) not on the total pressure, P. This leads to the well-known principle of Le Chatelier. Consider a gas reaction like:

\[A \rightleftharpoons B + C \nonumber \nonumber \]

e.g.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

In pressures, the equilibrium constant becomes:

$$K = \frac{P_B P_C}{P_A}$$

If initially n_A =1 we have at an extent ξ:

n_A = 1- ξ
n_B= ξ
n_C= ξ

n_{Total} = 1+ ξ

The partial pressures are given by Dalton's law:

P_A= [1- ξ /1+ ξ] P
P_B [ξ / 1+ ξ] P
P_C [ξ /1+ ξ] P

The equilibrium constant becomes:

$$K = P\frac{\xi_{eq}^2}{1-\xi_{eq}^2}$$

Even though the total pressure, P, does occur in this equation, K is *not* dependent on P. If the total pressure is changed (e.g. by compression of the gas) the value of ξ_{eq} will change (the equilibrium shifts) in response. It will go to the side with the fewer molecules. This fact is known as le Chatelier's principle

If the system is not ideal we will also get a Chatelier shift, but the value of K may change a little because the value of the activity coefficients (or fugacity) is a little dependent on the pressure too. In solution the same thing holds. In ideal solutions K is only T dependent, but as we saw these systems are rare. Particularly in ionic solutions equilibrium constants will be effected by other things than just temperature, e.g. changes in the ionic strength and we need to find the activity coefficients to make any predictions.

✓ Example

Consider the reaction of ammonia decomposition:

$$2\text{NH}_3\,(g) \leftrightharpoons \text{N}_2\,(g) + 3\text{H}_2\,(g)$$

$$\Delta_f H^\circ(\text{NH}_3, g) = -45.90\ \text{kJ/mol}$$

The reaction is initially at equilibrium. For each of the stresses, use your General Chemistry knowledge to decide if equilibrium will be unaffected, or if it will shift towards reactants or products.

Process	Shifts towards
Isothermal removal of H_2 gas	
Isothermal addition of N_2 gas	
Isothermal decrease of container volume	
Isothermal and isochoric addition of argon gas	
Isobaric increase of temperature	

Write the equilibrium constant expression for the above chemical reaction in terms of gas-phase mole fractions.

7.3.2: Concentration

The gas law contains a hidden definition of concentration:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = cRT$$

$$c = \frac{P}{RT} \tag{7.3.1}$$

Here c stands for the molar amount per unit volume or ***molarity***. For gaseous mixtures we do not use this fact much, but it provides the link to the more important liquid solution as a reaction medium. We can rewrite the equilibrium constant as

$$K = \frac{c_{eq,Y}^{v_Y} c_{eq,Z}^{v_Z}}{c_{eq,A}^{v_A} c_{eq,B}^{v_B}} \tag{7.3.2}$$

However, c (Equation 7.3.1) is substituted into K (Equation 7.3.2), then not all the factors of RT cancel. The missing term g. ln[RT] depends on the stoichiometric coefficients:

$$g = v_Y + v_Z - v_A - v_B$$

The term is generally *incorporated* in $\Delta_r G^{\ominus}$ so that the latter now refers to a new standard state of 1 mole per liter of each species rather than 1 bar of each (or so).

7.4: Pressure Dependence of Kp - Le Châtelier's Principle

Since the equilibrium constant K_p is a function of ΔG^o_{rxn} which is defined for a specific composition (all reactants in their standard states and at unit pressure (or fugacity), changes in pressure have no effect on equilibrium constants for a fixed temperature. However, changes in pressure can have profound effects on the compositions of equilibrium mixtures.

To demonstrate the relationship, one must recall Dalton's law of partial pressures. According to this relationship, the partial pressure of a component of a gas-phase mixture can be expressed

$$p_i = \chi_t p_{tot}$$

It is the combination of mole fractions that describes the composition of the equilibrium mixture.

Substituting the above expression into the expression for K_p yields

$$K_p = \prod_i (\chi_i p_{tot})^{\nu_i}$$

This expression can be factored into two pieces – one containing the mole fractions and thus describing the composition, and one containing the total pressure.

$$K_p = \left(\prod_i \chi_i^{\nu_i}\right)\left(\prod_i p_{tot}^{\nu_i}\right)$$

The second factor is a constant for a given total pressure. If the first term is given the symbol K_x, the expression becomes

$$K_p = K_x (p_{tot})^{\sum_i \nu_i}$$

In this expression, K_x has the same form as an equilibrium constant

$$K_x = \prod \chi_i^{\sum_i \nu_i}$$

but is not itself a constant. The value ofK_x will vary with varying composition, and will *need* to vary with varying total pressure (in most cases) in order to maintain a constant value of K_p.

✓ Example 7.4.1:

Consider the following reaction at equilibrium.

$$A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$$

In which direction will the equilibrium shift if the volume of the reaction vessel is decreased?

Solution

A decrease in the volume will lead to an increase in total pressure. Since the equilibrium constant can be expressed as

$$K_p = \frac{p_c p_D}{p_A p_B^2} = \frac{\chi_p \chi_D}{\chi_A \chi_B^2}(p_{tot})^{-1}$$

An increase in pressure will lead to an increase in K_x to maintain a constant value of K_p. So the reaction will shift to form more of the products C and D.

Note: This should make some sense, since a shift to the side of the reaction with fewer moles of gas will lower the total pressure of the reaction mixture, and thus relieving the stress introduced by increasing the pressure. This is exactly what is expected according to Le Chatelier's principle.

It should be noted that there are several ways one can affect the total pressure of a gas-phase equilibrium. These include the introduction or removal of reactants or products (perhaps through condensation or some other physical process), a change in volume of the reaction vessel, or the introduction of an inert gas that does not participate in the reaction itself. (Changes in the temperature will be discussed in a later section.) The principle of Le Chatelier's can be used as a guide to predict how the equilibrium composition will respond to a change in pressure.

> *Le Chatelier's principle: When a stress is introduced to a system at equilibrium, the system will adjust so as to reduce the stress.*

Le Chatlier's principle is fairly clear on how to think about the addition or removal of reactants or products. For example, the addition of a reactant will cause the system to shift to reduce the partial pressure of the reactant. It can do this by forming more products.

An important exception to the rule that increasing the total pressure will cause a shift in the reaction favoring the side with fewer moles of gas occurs when the total pressure is increased by introducing an inert gas to the mixture. The reason is that the introduction of an inert gas will affect the total pressures *and* the partial pressures of each individual species.

✓ Example 7.4.2:

A 1.0 L vessel is charged with 1.00 atm of A, and the following reaction is allowed to come to equilibrium at 298 K.

$$A(g) \rightleftharpoons 2B(g)$$

with $K_p = 3.10$.

a. What are the equilibrium partial pressures and mole fractions of A and B?
b. If the volume of the container is doubled, what are the equilibrium partial pressures and mole fractions of A and B?
c. If 1.000 atm of Ar (an inert gas) is introduced into the system described in b), what are the equilibrium partial pressures and mole fractions of A and B once equilibrium is reestablished?

Solution

Part a:

First, we can use an ICE[1] table to solve part a).

	A	2 B
Initial	1.00 atm	0
Change	-x	+2x
Equilibrium	1.00 atm - x	2x

So (for convenience, consider K_p to have units of atm)

$$3.10\,atm = \frac{(2x)^2}{1.00\,atm - x}$$

Solving for x yields values of

$$x_1 = -1.349\,atm$$

$$x_1 = 0.574\,atm$$

Clearly, x_1, while a solution to the mathematical problem, is not physically meaningful since the equilibrium pressure of B cannot be negative. So the equilibrium partial pressures are given by

$$p_A = 1.00\,atm - 0.574\,atm = 0.426\,atm$$

$$p_B = 2(0.574\,atm) = 1.148\,atm$$

So the mole fractions are given by

$$chi_A = \frac{0.426\,atm}{0.426\,atm + 1.148\,atm} = 0.271$$

$$\chi_B = 1 - \chi_A = 1 - 0.271 = 0.729$$

Part b:

The volume is doubled. Again, an ICE table is useful. The initial pressures will be half of the equilibrium pressures found in part a).

	A	2 B
Initial	0.213 atm	0.574 atm
Change	-x	+2x
Equilibrium	0.213 atm - x	0.574 atm + 2x

So the new equilibrium pressures can be found from

$$3.10\,atm = \frac{(0.574\,atm + 2x)^2}{0.213\,atm - x}$$

And the values of x that solve the problem are

$$x_1 = -1.4077\,atm$$

$$x_1 = 0.05875\,atm$$

We reject the negative root (since it would cause both of the partial pressures to become negative. So the new equilibrium partial pressures are

$$p_A = 0.154\,atm$$

$$p_B = 0.0692\,atm$$

And the mole fractions are

$$\chi_A = 0.182$$

$$\chi_B = 0.818$$

We can see that the mole fraction of A decreased and the mole fraction B increased. This is the result expected by Le Chatlier's principle since the lower total pressure favors the side of the reaction with more moles of gas.

Part c:

We introduce 1.000 atm of an inert gas. The new partial pressures are

$$p_A = 0.154\,atm$$

$$p_B = 0.692\,atm$$

$$p_{Ar} = 1.000\,atm$$

And because the partial pressures of A and B are unaffected, the equilibrium does not shift! What *is* affected is the composition, and so the mole fractions will change.

$$\chi_A = \frac{0.154\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_B = \frac{0.692\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_{Ar} = \frac{1.000\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

And since

$$K_p = K_x(p_{tot})$$

$$\frac{(0.3749)^2}{0.08342}(1.846\,atm) = 3.1$$

> Within round-off error, the value obtained is the equilibrium constant. So the conclusion is that the introduction of an inert gas, even though it increases the total pressure, does not induce a change in the partial pressures of the reactants and products, so it does not cause the equilibrium to shift.

---

[1] ICE is an acronym for “Initial, Change, Equilibrium”. An ICE table is a tool that is used to solve equilibrium problems in terms of an unknown number of moles (or something proportional to moles, such as pressure or concentration) will shift for a system to establish equilibrium. See (Tro, 2014) or a similar General Chemistry text for more background and information.

7.5: Degree of Dissociation

Reactions such as the one in the previous example involve the dissociation of a molecule. Such reactions can be easily described in terms of the fraction of reactant molecules that actually dissociate to achieve equilibrium in a sample. This fraction is called the **degree of dissociation**. For the reaction in the previous example

$$A(g) \rightleftharpoons 2B(g)$$

the degree of dissociation can be used to fill out an ICE table. If the reaction is started with n moles of A, and a is the fraction of A molecules that dissociate, the ICE table will look as follows.

	A	$2B$
Initial	n	0
Change	$-\alpha n$	$+2n\alpha$
Equilibrium	$n(1-\alpha)$	$2n\alpha$

The mole fractions of A and B can then be expressed by

$$\begin{aligned} \chi_A &= \frac{n(1-\alpha)}{n(1-\alpha)+2n\alpha} \\ &= \frac{1-\alpha}{1+\alpha} \\ \chi_B &= \frac{2\alpha}{1+\alpha} \end{aligned}$$

Based on these mole fractions

$$K_x = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2}{\frac{1-\alpha}{1+\alpha}} \tag{7.5.1}$$

$$= \frac{4\alpha^2}{1-\alpha^2} \tag{7.5.2}$$

And so K_p, which can be expressed as

$$K_p = K_x (p_{tot})^{\sum \nu_i} \tag{7.5.3}$$

is given by

$$K_p = \frac{4\alpha^2}{(1-\alpha^2)}(p_{tot})$$

✓ Example 7.5.1

Based on the values given below, find the equilibrium constant at 25 °C and degree of dissociation for a system that is at a total pressure of 1.00 atm for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

	$N_2O_4(g)$	$NO_2(g)$
ΔG_f^o (kJ/mol)	99.8	51.3

Solution

First, the value of K_p can be determined from ΔG^o_{rxn} via an application of Hess' Law.

$$\Delta G^o_{rxn} = 2\,(51.3\,kJ/mol) - 99.8\,kJ/mol \qquad = 2.8\,kJ/mol$$

So, using the relationship between thermodynamics and equilibria

$$\Delta G^o_f = -RT\ln K_p$$

$$2800\,kJ/mol = -(8.314J/(mol\,K)(298\,K)\ln K_p$$

$$K_p = 0.323\,atm$$

The degree of dissociation can then be calculated from the ICE tables at the top of the page for the dissociation of $N_2O_4(g)$:

$$K_p = \frac{4\alpha^2}{1-\alpha^2}(p_{tot})$$

$$0.323\,atm = \frac{4\alpha^2}{1-\alpha^2}(1.00\,atm)$$

Solving for α,

$$\alpha = 0.273$$

Note: since a represents the fraction of N_2O_4 molecules dissociated, it **must** be a positive number between 0 and 1.

Example 7.5.2

Consider the gas-phase reaction

$$A + 2B \rightleftharpoons 2C$$

A reaction vessel is initially filled with 1.00 mol of A and 2.00 mol of B. At equilibrium, the vessel contains 0.60 mol C and a total pressure of 0.890 atm at 1350 K.

1. How many mol of A and B are present at equilibrium?
2. What is the mole fraction of A, B, and C at equilibrium?
3. Find values for K_x, K_p, and ΔG^o_{rxn}.

Solution

Let's build an ICE table!

	A	2 B	2 C
Initial	1.00 mol	2.00 mol	0
Change	-x	-2x	+2x
Equilibrium	1.00 mol - x	2.00 mol – 2x	2x = 0.60 mol

From the equilibrium measurement of the number of moles of C, x = 0.30 mol. So at equilibrium,

	A	2 B	2 C
Equilibrium	0.70 mol	1.40 mol	0.60 mol

The total number of moles at equilibrium is 2.70 mol. From these data, the mole fractions can be determined.

$$\chi_A = \frac{0.70\,mol}{2.70\,mol} = 0.259$$

$$\chi_B = \frac{1.40\,mol}{2.70\,mol} = 0.519$$

$$\chi_C = \frac{0.60\,mol}{2.70\,mol} = 0.222$$

So K_x is given by

$$K_x = \frac{(0.222)^2}{(0.259)(0.519)^2} = 0.7064$$

And K_p is given by Equation 7.5.3, so

$$K_p = 0.7604(0.890\, atm)^{-1} = 0.792\, atm^{-1}$$

The thermodynamic equilibrium constant is unitless, of course, since the pressures are all divided by 1 atm. So the actual value of K_p is 0.794. This value can be used to calculate ΔG^o_{rxn} using

$$\Delta G^o_{rxn} = -RT \ln K_p$$

so

$$\begin{aligned} \Delta G^o_{rxn} &= -(8.314\, J/(mol\, K))(1350\, K) \ln(0.792) \\ &= 2590\, J/mol \end{aligned}$$

7.6: The Dumas Bulb Method for Measuring Decomposition Equilibrium

A classic example of an experiment that is employed in many physical chemistry laboratory courses uses a Dumas Bulb method to measure the dissociation of $N_2O_4(g)$ as a function of temperature (Mack & France, 1934). In this experiment, a glass bulb is used to create a constant volume container in which a volatile substance can evaporate, or achieve equilibrium with other gases present. The latter is of interest in the case of the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{7.6.1}$$

The reaction is endothermic, so at higher temperatures, a larger degree of dissociation is observed.

The procedure is to first calibrate the internal volume of the Dumas bulb. This is done using a heavy gas (such as SF_6) and comparing the mass of the bulb when evacuated to the mass of the bulb full of the calibrant gas at a particular pressure and temperature.

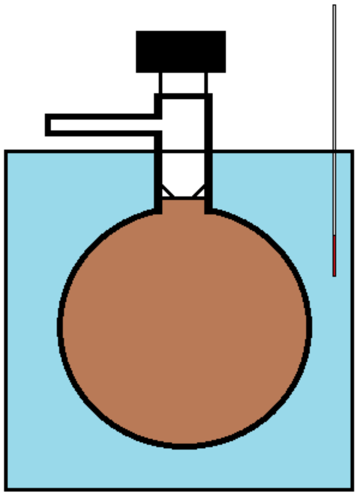


Figure 7.6.1:

The Dumas bulb is then charged with a pure sample of the gas to be investigated (such as N_2O_4) and placed in a thermalized bath. It is then allowed to come to equilibrium. Once Equilibrium is established, the stopcock is opened to allow gas to escape until the internal pressure is set to the pressure of the room. The stopcock is then closed and the bulb weighed to determine the total mass of gas remaining inside. The experiment is repeated at higher and higher temperatures (so that at each subsequent measurement, the larger degree of dissociation creates more molecules of gas and an increase in pressure in the bulb (along with the higher temperature), which then leads to the expulsion of gas when the pressure is equilibrated.

The degree of dissociation is then determined based on the calculated gas density at each temperature.

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2(n-1)}$$

where ρ_1 is the measured density and ρ_2 is the theoretical density if no dissociation occurs (calculated from the ideal gas law for the given temperature, pressure, and molar mass of the dissociating gas) and n is the number of fragments into which the dissociating gas dissociates (ie.g., $n = 2$ for Equation \req{eq1}). The equilibrium constant is then calculated as

$$K = \frac{4\alpha^2}{1-\alpha^2}\left(\frac{p}{1.00\,atm}\right)$$

Finally, a van't Hoff plot is generated to determine the reaction enthalpy.

7.7: Gibbs Energy of a Reaction vs. Extent of Reaction is a Minimum at Equilibrium

As discussed in Section 26.4, we defined the extent of the reaction (ξ) as a quantitative measure of how far along the reaction has evolved. For simple reactions like $\mathrm{A} \rightleftharpoons \mathrm{B}$, the extent of reaction is easy to define and is simply the number of moles of A that has been converted to B. Since $d\xi$ has the same value as dn, we can write that

$$\begin{aligned} dG &= \mu_A dn_A + \mu_B dn_B \\ &= -\mu_A d\xi + \mu_B d\xi. \end{aligned}$$

The minus sign comes from the fact that when the reaction goes in the left to right direction, the amount of A is decreasing, while the amount of B is increasing. Looking at these equations, it is reasonable to suggest that:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = \mu_B - \mu_A$$

This is the slope of the free energy with respect to the extent of the reaction. This relationship will have a region where the sign is negative, one point where the value is zero and a region where the value is positive (Figure $7.7.1$). If we look at a plot of G as a function of ξ, we can see that the point where is the minimum of the curve:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = 0$$

This is the point where μ_A and μ_B are the same. On one side of the minimum, the slope is negative and on the other side, the slope is positive. In both cases, the reaction is spontaneous (i.e, $dG < 0$) as long as the reaction is evolving towards the minimum, which will be called the **equilibrium position**. Hence, all reactions spontaneously move towards equilibrium; the immediate question is what value of ξ corresponds to the equilibrium position of a reaction?

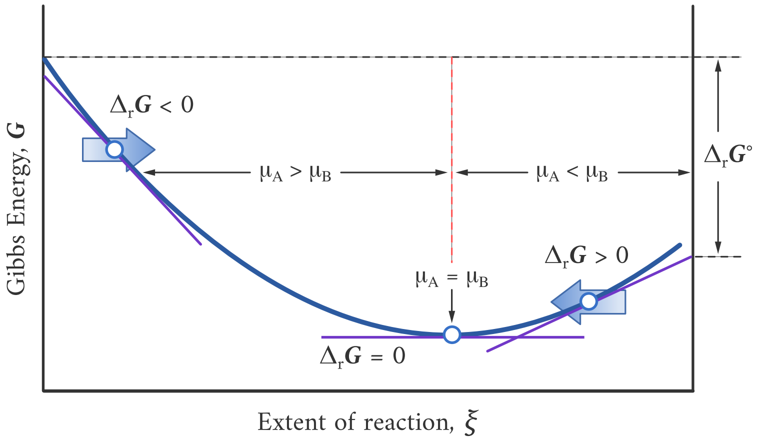


Figure $7.7.1$: Reactive Gibbs Energy and Equilibria. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Terminology

- A reaction for which $\Delta_r G < 0$ is called **exergonic**.
- A reaction for which $\Delta_r G > 0$ is called **endergonic**.
- $\Delta_r G < 0$, the forward reaction is spontaneous.
- $\Delta_r G > 0$, the reverse reaction is spontaneous.
- $\Delta_r G = 0$, the reaction is at equilibrium.

7.7.1: Ideal Gas Equilibrium

To understand how we can find the minimum and what the Gibbs free energy of a reaction depends on, let's first start with a reaction that converts one ideal gas into another.

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

Let's assume the reaction enthalpy is zero and hence the only thing that determines what the ratio of product to reactant should be is the entropy term (the mixing term), which is the most favorable when the mixture is half and half.

$$\Delta G_{\text{mix}} = nRT\left(\chi_A \ln \chi_A + \chi_B \ln \chi_B\right) \tag{7.7.1}$$

Remember that the Gibbs free energy of mixing is not a molar quantity and depends on n (unlike the reaction Gibbs free energy). Also, the Gibbs free energy of mixing is defined relative to pure A and B. The free energy of mixing in Equation 7.7.1 is at a minimum when the amounts of A equal B.

Thus, if we have a reaction $\mathrm{A} \rightleftharpoons \mathrm{B}$ and there is no enthalpy term (and no change in the inherent entropy of A vs. B), we would expect the system to have the minimum Gibbs free energy when the mole fraction of A and B are each 0.5.

Think about it

If A can form B and B can form A and there is no other forces involved (no heat/enthalpy) that would favor one product over the other, probability would just state that eventually you will have statistically the same amount of both A and B present -- this is the lowest free energy state. (This, of course, will not be true if the enthalpy for the reaction is not zero or if A and B have different inherent entropies). Usually there are additional terms for the reaction.

Lets work through this for an ideal gas reaction:

$$\begin{aligned}
\Delta_r G &= \mu_B - \mu_A \\
&= \mu_B^o + RT \ln \frac{P_B}{P^\theta} - \mu_A^o - RT \ln \frac{P_A}{P^\theta} \\
&= \mu_B^o - \mu_A^o + RT \ln \frac{P_B}{P_A}
\end{aligned}$$

What we normally do at this point is to give the first two terms a special name. Since it is the difference between the chemical potentials at standard conditions, we refer to it as the Gibbs free energy of reaction at standard conditions or the **standard Gibbs free energy of reaction**.

$$\Delta_r G^o = \mu_B^o - \mu_A^o$$

$$\Delta_r G = \Delta_r G^o + RT \ln \frac{P_B}{P_A} \tag{7.7.2}$$

There are two parts to Equation 7.7.2. The first term ($\Delta_r G^o$) is the Gibbs free energy for converting one mole of A to B under standard conditions (1 bar of both A and B). The second term is the mixing term that is minimized when the amounts of A and B are equal to one another (Figure 7.7.2). The first term you look up in a reference book and is specific for a specific reaction. The second term is calculated knowing the partial pressures of A and B in the gas.

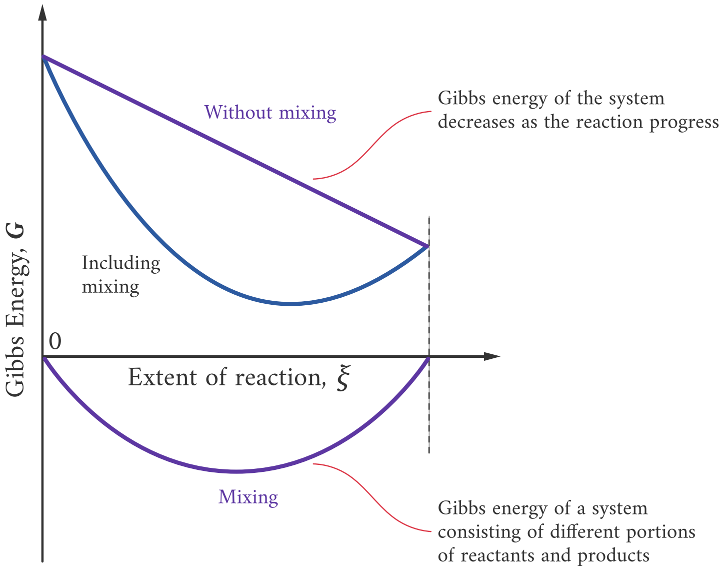


Figure 7.7.2: Molecular interpretation of the minimum in the reaction Gibbs energy Gibbs energy of the system decreases as the reaction progress Gibbs energy of a system consisting of different portions of reactants and products. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Now the minimum absolute Gibbs free energy will occur at the bottom of the curve where the slope is zero. Thus, the lowest free energy will occur when the reaction free energy (i.e., the slope of that curve in Figure 7.7.1) is equal to zero. The chemical potentials of A and B are equal.

$$\mu_A = \mu_B$$

At this point, the reaction will neither go forwards or backwards and we call this equilibrium. Hence, at equilibrium:

$$\begin{aligned}\Delta_r G &= \Delta_r G^o + RT \ln \frac{P_B}{P_A} \\ &= 0\end{aligned}$$

and the specific ratio of P_A and P_B necessary to ensure $\Delta_r G = 0$ is characteristic of the reaction and is called the **equilibrium constant** for that reaction.

$$K_{eq} = \frac{P_B}{P_A}$$

We can now relate thermodynamic quantities to concentrations of molecules at equilibrium. We can also see that at equilibrium:

$$\begin{aligned}0 &= \Delta_r G^o + RT \ln K_{eq} \\ \Delta_r G^o &= -RT \ln K_{eq} \\ K_{eq} &= e^{-\frac{\Delta_r G^o}{RT}}\end{aligned}$$

7.8: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity

It is important to distinguish between the Gibbs energy of reaction, $\Delta_r G$ and the standard state Gibbs energy of reaction, $\Delta_r G^{\circ}$. The $^{\circ}$ refers to standard state conditions. That is, each reactant and product has a partial pressure of 1 bar if a gas, a concentration of 1 M if a solution, and they are all unmixed from each other. Such idealized conditions, while convenient for serving as a reference state, do not actually represent real reaction conditions. Consider the reaction of nitrogen with hydrogen to form ammonia:

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

$$\Delta_r G^{\circ} = -32.9\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

If the reaction was run under standard state conditions (1 bar partial pressure of each gas), the reaction would shift towards the products since $\Delta_r G^{\circ} < 0$. That is, the partial pressures of N_2 and O_2 will decrease and the partial pressure of NH_3 will increase until equilibrium is reached. The Gibbs energy of reaction is dependent on the composition:

$$\Delta_r G = \Delta_r G^{\circ} + RT\ln Q = \Delta_r G^{\circ} + RT\ln\left(\frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}} P_{\mathrm{H_2}}^3}\right)$$

At equilibrium, the minimum Gibbs energy of reaction will be reached:

$$\Delta_r G = 0\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

And the reaction quotient will equal the equilibrium constant:

$$Q = K$$

- **26.6: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity** is licensed CC BY-NC-SA 4.0.

7.9: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction

The Gibbs free energy function was constructed to be able to predict which changes could occur spontaneously. If we start with a set of initial concentrations we can write them in a reaction quotient

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

if we subtract the equilibrium version of this expression:

$$0 = \Delta_r G^o + RT \ln K$$

we get

$$\Delta_r G = RT \ln \left(\frac{Q}{K} \right)$$

That gives us the sign of $\Delta_r G$. If this is negative the reaction will spontaneously proceed from left to right as written, if positive it will run in reverse. In both case the value of Q will change until $Q = K$ and equilibrium has been reached.

The main difference between K and Q is that K describes a reaction that is at equilibrium, whereas Q describes a reaction that is not at equilibrium. To determine Q, the concentrations of the reactants and products must be known. For a given general chemical equation:

$$aA + bB \rightleftharpoons cC + dD \tag{7.9.1}$$

the Q equation is written by multiplying the activities for the species of the products and dividing by the activities of the reactants. If any component in the reaction has a coefficient, indicated above with lower case letters, the concentration is raised to the power of the coefficient. Q for the above equation is therefore:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{7.9.2}$$

Note

A comparison of Q with K indicates which way the reaction shifts and which side of the reaction is favored:

- If $Q > K$, then the reaction favors the reactants. This means that in the Q equation, the ratio of the numerator (the concentration or pressure of the products) to the denominator (the concentration or pressure of the reactants) is larger than that for K, indicating that more products are present than there would be at equilibrium. Because reactions always tend toward equilibrium (Le Châtelier's Principle), the reaction produces more reactants from the excess products, therefore causing the system to shift to the **LEFT.** This allows the system to reach equilibrium.
- If $Q < K$, then the reaction favors the products. The ratio of products to reactants is less than that for the system at equilibrium—the concentration or the pressure of the reactants is greater than the concentration or pressure of the products. Because the reaction tends toward reach equilibrium, the system shifts to the **RIGHT** to make more products.
- If $Q = K$, then the reaction is already at equilibrium. There is no tendency to form more reactants or more products at this point. No side is favored and no shift occurs.

7.10: The van 't Hoff Equation

We can use Gibbs-Helmholtz to get the temperature dependence of K

$$\left(\frac{\partial[\Delta G^o/T]}{\partial T}\right)_P = \frac{-\Delta H^o}{T^2}$$

At equilibrium, we can equate ΔG^o to $-RT\ln K$ so we get:

$$\left(\frac{\partial[\ln K]}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2}$$

We see that whether K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative. If temperature is changed little enough that ΔH^o can be considered constant, we can translate a K value at one temperature into another by integrating the above expression, we get a similar derivation as with melting point depression:

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

If more precision is required we could correct for the temperature changes of ΔH^o by using heat capacity data.

> *How K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative.*

The expression for K is a rather sensitive function of temperature given its exponential dependence on the difference of stoichiometric coefficients One way to see the sensitive temperature dependence of equilibrium constants is to recall that

$$K = e^{-\Delta_r G^o/RT} \tag{7.10.1}$$

However, since under constant pressure and temperature

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Equation 7.10.1becomes

$$K = e^{-\Delta H^o/RT} e^{\Delta S^o/R} \tag{7.10.2}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \tag{7.10.3}$$

which is known as the van 't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.

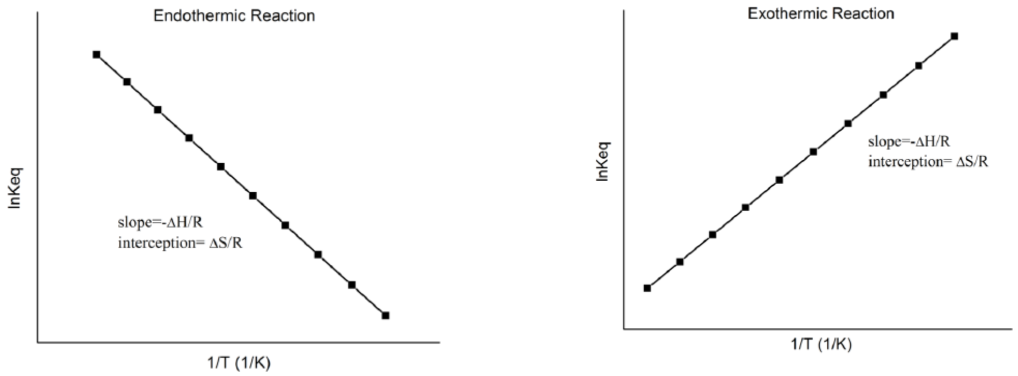


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

Hence, these quantities can be determined from the $\ln K$ vs. $1/T$ data without doing calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on T, which is usually valid.

CHAPTER OVERVIEW

8: Electrochemistry

8.1: Electrolytes Solutions are Nonideal at Low Concentrations

A solution with a strong electrolyte, such as NaCl in water, is perhaps one of the most obvious systems to consider but, unfortunately, is also one of the more difficult ones. The reason is that the electrolyte produces two ***charged*** solutes, Na^+ and Cl^+ (both in hydrated form), in solution. We need to consider the dissociation process and stoichiometry as we are bringing more than one solute species into solution. We also need to consider electrostatic interactions between solutes. The charges introduce a strong interaction that falls off with r^{-1}, as opposed to ~r^{-6} if only neutral species are present. This causes a very serious divergence from ideality even at very low concentrations. Consider a salt going into solution:

$$C_{\nu_+}A_{\nu_-} \rightarrow \nu_+ C^{z+} + \nu_- A^{z-} \tag{8.1.1}$$

where ν_+ and ν_- are the ***stoichiometric coefficients*** and z_+ and z_- are the formal charges of the cation and anion, respectively. As we shall see, the stoichiometric coefficients involved in the dissociation process are important for a proper description of the thermodynamics of strong electrolytes. Charge neutrality demands:

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{8.1.2}$$

8.1.1: Thermodynamic potentials versus the dissociation

For the salt, we can write:

$$\mu_2 = \mu_2^o + RT \ln a_2 \tag{8.1.3}$$

However, we need to take into account the dissociation of the salt. To do so, we write:

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_- \tag{8.1.4}$$

This implies:

$$\mu_2^o = \nu_+ \mu_+^o + \nu_- \mu_-^o \tag{8.1.5}$$

where

$$\mu_+ = \mu_-^o + RT \ln a_+ \tag{8.1.6}$$

$$\mu_- = \mu_-^o + RT \ln a_- \tag{8.1.7}$$

Usually Henry's law is taken as standard state for both type of ions. However, we cannot measure the activities of the ions separately as it is impossible to add one without adding the other. Nevertheless, we can derive a useful formalism that takes into account the dissociation process. If we substitute the last two equations in the ones above we get:

$$\nu_+ \ln a_+ + \nu_- \ln a_- = \ln a_2 \tag{8.1.8}$$

Taking the exponent of either side of Equation 8.1.8, we get:

$$a_2 = a_+^{\nu_+} a_-^{\nu-} \tag{8.1.9}$$

Notice that the stoichiometric coefficients (Equation 8.1.1) are *exponents* in Equation 8.1.9. We now introduce the sum of the stoichiometric coefficients:

$$\nu_+ + \nu_- = \nu \tag{8.1.10}$$

and *define* the ***mean ionic activity*** $a_\pm$ as:

$$a_\pm^\nu \equiv a_2 = a_+^{\nu+} a_-^{\nu-}$$

Note

The mean ionic activity $a_\pm$ and the activity of the salt are closely related but the relationship involves *exponents* due to stoichiometric coefficients involved in the dissociation process. For example:

- For Na_1Cl_1: ν= 1+1 = **2:** $a_\pm{}^2 = a_{NaCl}$
- For $Al_2(SO_4)_3$: ν= 2+3 = **5:** $a_\pm{}^5 = a_{Al_2(SO_4)_3}$

8.1.2: Activity coefficients

All this remains a formality unless we find a way to relate it back to the concentration of the salt. Usually *molality* is used as a convenient concentration measure rather than molarity because we are dealing with pretty strong deviations from ideal behavior and that implies that volume may not be an additive quantity. Molality does not involve volume in contrast to molarity. Working with molalities, we can define activity coefficients for both ions, even though we have no hope to determine them separately:

$$a_{+}=\gamma_{+}m_{+} \tag{8.1.11}$$

$$a_{-}=\gamma_{-}m_{-} \tag{8.1.12}$$

Stoichiometry dictates the molalities of the individual ions must be related to the ***molality of the salt*** m by:

$$m_{-}=\nu_{-}m \tag{8.1.13}$$

$$m_{+}=\nu_{+}m \tag{8.1.14}$$

Note

We cannot measure the activities of the ions separately because it is impossible to add one without adding the other

Analogous to the mean ionic activity, we can define a **mean ionic molality** as:

$$m_{\pm}^{\nu}\equiv m_{+}^{\nu+}m_{-}^{\nu-} \tag{8.1.15}$$

We can do the same for the **mean ionic activity coefficient**:

$$\gamma_{\pm}^{\nu}=\gamma_{+}^{\nu+}\gamma_{-}^{\nu-} \tag{8.1.16}$$

Using this definitions we can rewrite:

$$a_{2}=a_{\pm}^{\nu}=a_{+}^{\nu+}a_{-}^{\nu-} \tag{8.1.17}$$

as:

$$a_{2}=a_{\pm}^{\nu}=\gamma_{\pm}^{\nu}m_{\pm}^{\nu} \tag{8.1.18}$$

Note

Note that when preparing a salt solution of molality m, we should ***substitute***:

$$m_{-}=\nu_{-}m$$

$$m_{+}=\nu_{+}m$$

into:

$$m_{\pm}^{\nu}\equiv m_{+}^{\nu+}m_{-}^{\nu-}$$

Example 25.5.1: Aluminum Sulfate

For $Al_2(SO_4)_3$ we get:

- $\nu = 2+3 = \mathbf{5}$
- $a_{\pm}^{\mathbf{5}} = a_{Al_2(SO_4)_3}$
- $m_{-}=3m$
- $m_{+}=2m$

So:

$$m_{\pm}^{\nu}=m_{+}^{\nu_{+}}m_{-}^{\nu_{-}}=(2m)^2(3m)^3=\mathbf{108}m^{\mathbf{5}}$$

$$a_{Al_2(SO_4)_3}=a_{\pm}^{\mathbf{5}}=\mathbf{108}m^{\mathbf{5}}\gamma_{\pm}^{5}$$

> As you can see the stoichiometry enter *both* into the exponents *and* into the calculation of the molality. Notice that the activity of the salt now goes as the fifth power of its overall molality (on top of the dependency of $\gamma_\pm$ of exp(√m) as shown below).

8.1.3: Measuring mean ionic activity coefficients

In contrast to the individual coefficients, the ***mean ionic activity coefficient*** $\gamma_\pm$ is a quantity that ***can be determined***. In fact we can use the same Gibbs-Duhem trick we did for the sucrose problem to do so. We simply measure the water vapor pressure above the salt solution and use:

$$\ln \gamma_\pm = \varphi - 1 + \int_{m'=0}^{m} [\varphi - 1] m'\, dm'$$

The fact that the salt itself has a negligible vapor pressure does not matter. Particularly for ions with high charges, the deviations from ideality are very strong even at tiny concentrations. Admittedly doing these vapor pressure measurements in pretty tedious, there are some other procedures involving electrochemical potentials. However, they too are tedious.

8.2: The Debye-Hückel Theory

As ionic solutions are very common in chemistry, having to measure all activity coefficients ($\gamma_{\pm}$) for all possible solute-solvent combinations is a pretty daunting task, even though in times past extensive tabulation has taken place. We should be grateful for the rich legacy that our predecessors have left us in this respect (it would be hard to get any funding to do such tedious work today). Of course, it would be very desirable to be able to *calculate* $\gamma_{\pm}$ values from first principles or if that fails by semi-empirical means. Fortunately, considerable progress has been made on this front as well. We can only scratch the surface of that topic in this course and will briefly discuss the simplest approach due to Debye and Hückel

Debye and Hückel came up with a theoretical expression that makes is possible to predict mean ionic activity coefficients as *sufficiently* dilute concentrations. The theory considers the vicinity of each ion as an atmosphere-like cloud of charges of opposite sign that cancels out the charge of the central ion (Figure $8.2.1$). From a distance the cloud looks neutral. The quantity $1/\kappa$ is a measure for the size of this cloud and κ is the ***Debye-length***. Its size depends on the concentration of all other ions.

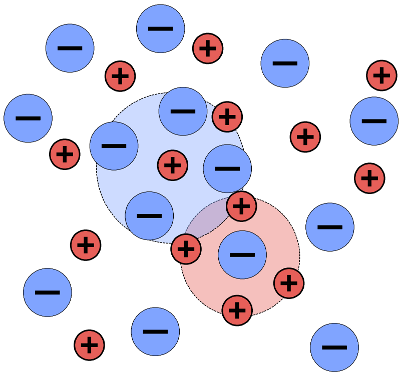


Figure $8.2.1$: An idealized representation of a solution of a 1:1 electrolyte. (CC BY-SA 3.0 unported; Roland1952 via Wikipedia)

8.2.1: Ionic Strength

To take the effect from all other ions into account, it is useful to define the ***ionic strength*** (I) as:

$$I = \frac{1}{2} \sum m_i z_i^2$$

where m_i is the molality of ion i and z_i is its charge coefficient. Note that highly charged ions (e.g. $z = 3+$) contribute strongly (nine times more than +1 ions), but the formula is *linear* in the molality. Using the ionic strength the Debye-length becomes:

$$\kappa^2 = constant\, I$$

The constant contains kT and $\varepsilon_r \varepsilon_o$ in the denominator and the number of Avogadro N_A and the square of the charge of the electron e in the numerator:

$$constant = 2000 \frac{e^2 N_A}{\varepsilon_r \varepsilon_o kT}$$

The Debye length and the logarithmic mean ionic activity coefficient are proportional:

$$\ln \gamma_{\pm} \propto \kappa$$

Again there are a number of factors in the proportionality constant:

$$\ln \gamma_{\pm} = -|q_+ q_-| \frac{\kappa}{8\pi \varepsilon_r \varepsilon_o kT}$$

Note

The factors ε_r and ε_o are the relative permittivity of the medium and the permittivity of vacuum, respectively. Note that the factor $8\pi\varepsilon_r\varepsilon_o$ is *specific* to the SI system of units. In cgs units the expression would look different, because the permittivities are defined differently in that system

If there is only one salt being dissolved, the ionic strength depends linearly on its concentration, the Debye length κ and $\ln \gamma_{\pm}$, therefore, go as the *square root of concentration* (usually molality):

$$\ln \gamma_{\pm} \propto \sqrt{m}$$

If there are other ions present the ionic strength involves *all* of them. This fact is sometimes used to keep ionic strength constant while changing the concentration of one particular ion. Say we wish to lower the concentration of Cu^{2+} in a redox reaction but we want to keep activity coefficients the same as much as possible. We could then *replace* it by an ion of the same charge say Zn^{2+} that does not partake in the reaction. A good way to do that is to dilute the copper solution with a zinc solution of the same concentration instead of with just solvent. The mean activity coefficient is given by the logarithm of this quantity as follows:

$$\log_{10} \gamma_{\pm} = -A z_j^2 \frac{\sqrt{I}}{1 + B a_0 \sqrt{I}} \tag{8.2.1}$$

with:

$$A = \frac{e^2 B}{2.303 \times 8\pi \epsilon_0 \epsilon_r k_{\mathrm{B}} T} \tag{8.2.2}$$

$$B = \left(\frac{2e^2 N}{\epsilon_0 \epsilon_r k_{\mathrm{B}} T} \right)^{1/2} \tag{8.2.3}$$

where I is the ionic strength and a_0 is a parameter that represents the distance of closest approach of ions. For aqueous solutions at 25 °C $A = 0.51\, mol^{-1}/2dm^{3/2}$ and $B = 3.29 nm^{-1} mol^{-1}/2dm^{3/2}$.

Unfortunately this theory only works at very low concentrations and is therefore also known as the **Debye limiting law** (Figure 8.2.2). There are a number of refinements that aim at extending the range of validity of the theory to be able to work at somewhat higher concentrations. These are discussed in the next section.

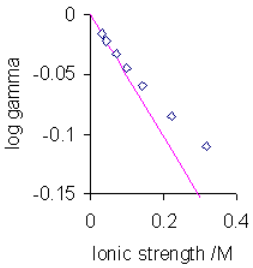


Figure 8.2.2: Experimental $\log \gamma_{\pm}$ values for KBr at 25°C (points) and Debye–Hückel limiting law (coloured line) (Public Domain; Petergans via Wikipedia)

The most significant aspect of Equation 8.2.1 is the prediction that the mean activity coefficient is a function of *ionic strength* rather than the electrolyte concentration. For very low values of the ionic strength the value of the denominator in the expression above becomes nearly equal to one. In this situation the mean activity coefficient is proportional to the square root of the ionic strength.

Importance for Colloids

When a solid is formed by a reaction from solution it is sometimes possible that it remains dispersed as very small particles in the solvent. The sizes typically range in the nanometers This is why it has become fashionable to call them *nanoparticles*, although they had been known as *colloidal particles* since the mid nineteenth century. They are smaller than the wavelength of the visible reason. This causes liquids that contain them to remain *clear*, although they can at times be beautifully colored. A good example is the reduction of $AuCl_4^-$ with citrate to metallic gold. This produces clear wine red solutions, even at tiny gold concentrations.

$$2\,\mathrm{nAuCl_4(aq)^-} + \mathrm{n\,citrate^{3-}(aq)} + 2\,\mathrm{n\,H_2O(l)} \rightarrow$$
$$2\,\mathrm{n\,Au(colloid)} + 3\,\mathrm{n\,CH_2O(aq)} + 3\,\mathrm{n\,CO_2(g)} + 8\,\mathrm{n\,Cl^-(aq)} + 3\,\mathrm{n\,H^+(aq)}$$

The reason the gold does not precipitate completely is typically that the nanoparticle (AuNP) formed during the reaction are *charged* by the attachment of some of the ionic species in solution to its surface. This results in an charged particle with an atmosphere with a certain Debye length around it (Figure 8.2.3). This charged cloud prevents the particle form coalescing with other particles by electrostatic repulsion.

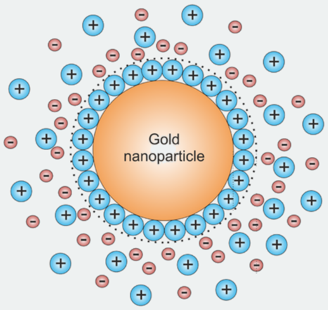


Figure 8.2.3: Potential difference as a function of distance from gold nanoparticle surface. (CC-SA-BY-3.0; Larryisgood)

Such a system is called a ***colloid.*** Of course these systems are ***metastable***. Often they have a pretty small threshold to crashing to a real precipitate under influence of the strong van der Waals interactions that the particles experience once they manage to get in close contact. Under the right conditions colloids can survive for a long time. Some gold colloids prepared by Faraday in the 1850's are still stable today.

It will be clear from the above that addition of a salt -particularly containing highly charged ions like 3+ or 3-- may destabilize the colloid because the ionic strength will changed drastically and this will affect the Debye length.

8.3: Extending Debye-Hückel Theory to Higher Concentrations

The equation for log $\gamma_{\pm}$ predicted from Debye–Hückel limiting law is:

$$\log_{10}\gamma_{\pm} = -Az_j^2\frac{\sqrt{I}}{1+Ba_0\sqrt{I}} \tag{8.3.1}$$

It gives satisfactory agreement with experimental measurements for low electrolyte concentrations, typically less than $10^{-3} mol/L$. Deviations from the theory occur at higher concentrations and with electrolytes that produce ions of higher charges, particularly asymmetrical electrolytes. These deviations occur because the model is oversimplified, so there is little to be gained by making small adjustments to the model. Instead, we must challenge the individual assumptions of the model:

- **Ions do not interact with each other**. Ion association may take place, particularly with ions of higher charge. This was followed up in detail by Niels Bjerrum. The Bjerrum length is the separation at which the electrostatic interaction between two ions is comparable in magnitude to kT.
- **Complete dissociation**. A weak electrolyte is one that is not fully dissociated. As such it has a dissociation constant. The dissociation constant can be used to calculate the extent of dissociation and hence, make the necessary correction needed to calculate activity coefficients.
- **Ions are spherical point charges that cannot be polarizable**. Ions, as all other atoms and molecules, have a finite size. Many ions, such as the nitrate ion $\mathrm{NO_3^-}$, are not spherical. Polyatomic ions are polarizable.
- **The solvent composition does not matter**. The solvent is not a structureless medium but is made up of molecules. The water molecules in aqueous solution are both dipolar and polarizable. Both cations and anions have a strong primary solvation shell and a weaker secondary solvation shell. Ion–solvent interactions are ignored in Debye–Hückel theory.
- **Ionic radius is negligible**. At higher concentrations, the ionic radius becomes comparable to the radius of the ionic atmosphere.

Most extensions to the Debye–Hückel theory are empirical in nature. They usually allow the Debye–Hückel equation to be followed at low concentration and add further terms in some power of the ionic strength to fit experimental observations. Several approaches have been proposed to extend the validity of the Debye–Hückel theory.

8.3.1: Extended Debye-Hückel Equation

One such approach is the Extended Debye-Hückel Equation:

$$-\log(\gamma) = \frac{A|z_+z_-|\sqrt{I}}{1+Ba\sqrt{I}} \tag{8.3.2}$$

where γ is the activity coefficient, z is the integer charge of the ion μ is the ionic strength of the aqueous solution, and a, is the size or effective diameter of the ion in angstrom. The effective hydrated radius of the ion, a is the radius of the ion and its closely bound water molecules. Large ions and less highly charged ions bind water less tightly and have smaller hydrated radii than smaller, more highly charged ions. Typical values are 3 Å for ions such as H+,Cl-,CN-, and HCOO-. The effective diameter for the hydronium ion is 9 Å. \ (A\) and B are constants with values of respectively 0.5085 and 0.3281 at 25°C in water.

Other approaches include the Davies equation, Pitzer equations and specific ion interaction theory.

8.3.2: Davis Equation

The Davies equation is an empirical extension of Debye–Hückel theory which can be used to calculate activity coefficients of electrolyte solutions at relatively high concentrations at 25 °C. The equation, originally published in 1938, was refined by fitting to experimental data. The final form of the equation gives the mean molal activity coefficient f± of an electrolyte that dissociates into ions having charges z1 and z2 as a function of ionic strength I:

$$-\log f_{\pm} = 0.5z_1z_2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.30I\right). \tag{8.3.3}$$

The second term, 0.30 I, goes to zero as the ionic strength goes to zero, so the equation reduces to the Debye–Hückel equation at low concentration. However, as concentration increases, the second term becomes increasingly important, so the Davies equation can be used for solutions too concentrated to allow the use of the Debye–Hückel equation. For 1:1 electrolytes the difference between measured values and those calculated with this equation is about 2% of the value for 0.1 M solutions. The calculations become less precise for electrolytes that dissociate into ions with higher charges. Further discrepancies will arise if there is association between the ions, with the formation of ion pairs, such as $Mg^{2+}SO_4^{2-}$.

Plot of activity coefficients calculated using the Davies equation.

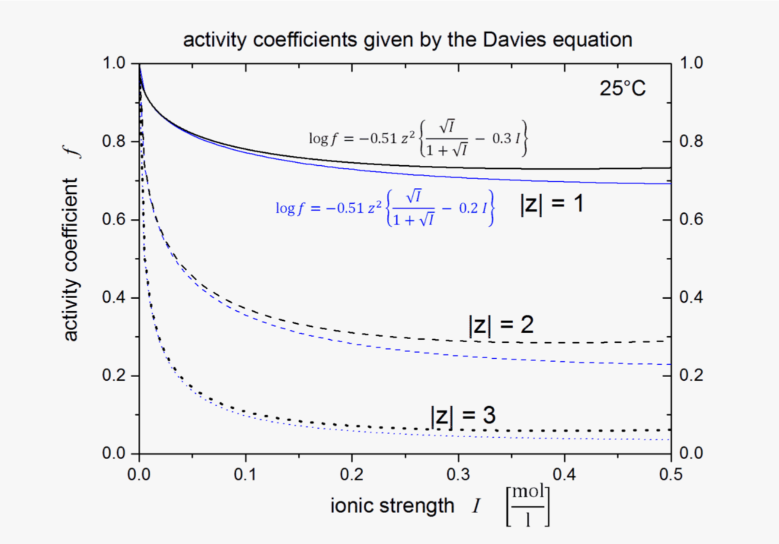


Figure 8.3.1: Semi-log plot of activity coefficients calculated using the Davies equation. (CC BY-SA 4.0; PChemiker via Wikipedia)

8.3.3: Pitzer Equations

Pitzer equations are important for the understanding of the behaviour of ions dissolved in natural waters such as rivers, lakes and sea-water. They were first described by physical chemist Kenneth Pitzer. The parameters of the Pitzer equations are linear combinations of parameters, of a virial expansion of the excess Gibbs free energy, which characterize interactions amongst ions and solvent. The derivation is thermodynamically rigorous at a given level of expansion. The parameters may be derived from various experimental data such as the osmotic coefficient, mixed ion activity coefficients, and salt solubility. They can be used to calculate mixed ion activity coefficients and water activities in solutions of high ionic strength for which the Debye–Hückel theory is no longer adequate.

An expression is obtained for the mean activity coefficient.

$$\ln \gamma_{\pm} = \frac{p \ln \gamma_M + q \ln \gamma_X}{p+q} \tag{8.3.4}$$

$$\ln \gamma_{\pm} = |z^+ z^-| f^{\gamma} + m \left(\frac{2pq}{p+q}\right) B^{\gamma}_{MX} + m^2 \left[2 \frac{(pq)^{3/2}}{p+q}\right] C^{\gamma}_{MX} \tag{8.3.5}$$

These equations were applied to an extensive range of experimental data at 25 °C with excellent agreement to about 6 mol kg−1 for various types of electrolyte. The treatment can be extended to mixed electrolytes and to include association equilibria. Values for the parameters β(0), β(1) and C for inorganic and organic acids, bases and salts have been tabulated. Temperature and pressure variation is also discussed.

8.3.4: Specific ion interaction theory

Specific ion Interaction Theory (SIT theory) is a theory used to estimate single-ion activity coefficients in electrolyte solutions at relatively high concentrations. It does so by taking into consideration interaction coefficients between the various ions present in solution. Interaction coefficients are determined from equilibrium constant values obtained with solutions at various ionic strengths. The determination of SIT interaction coefficients also yields the value of the equilibrium constant at infinite dilution.

The activity coefficient of the jth ion in solution is written as γ_j when concentrations are on the molal concentration scale and as yj when concentrations are on the molar concentration scale. (The molality scale is preferred in thermodynamics because molal concentrations are independent of temperature). The basic idea of SIT theory is that the activity coefficient can be expressed as

$$\log \gamma_j = -z_j^2 \frac{0.51\sqrt{I}}{1+1.5\sqrt{I}} + \sum_k \epsilon_{jk} m_k \tag{8.3.6}$$

where z is the electrical charge on the ion, I is the ionic strength, ε and b are interaction coefficients and m are concentrations. The summation extends over the other ions present in solution, which includes the ions produced by the background electrolyte. The first term in these expressions comes from Debye-Hückel theory. The second term shows how the contributions from "interaction" are dependent on concentration. Thus, the interaction coefficients are used as corrections to Debye-Hückel theory when concentrations are higher than the region of validity of that theory.

8.4: Electricity

Electricity has been known for some time. Ancient Egyptians, for example, referred to electric fish in the Nile River as early as 2750 BC (Moller & Kramer, 1991). In 1600, William Gilbert studied what would later be seen to be electrostatic attraction, by creating static charges rubbing amber (Stewart, 2001). And Benjamin Franklin's famous experiment (although it is actually uncertain if he performed the experiment) of attaching a metal key to a kite string occurred in 1752, and showed that lightening is an electrical phenomenon (Uman, 1987).

One of the biggest breakthroughs in the study of electricity as a chemical phenomenon was made by Alessandro Volta, who in 1799 showed that electricity could be generated by stacking copper and zinc disks submerged in sulfuric acid (Routledge, 1881). The reactions that Volta produced in his **voltaic pile** included both **oxidation** and **reduction** processes that could be considered as **half-reactions**. The half-reactions can be classified as **oxidation** (the loss of electrons) which happens at the **anode** and **reduction** (the gain of electrons) which occurs at the **cathode**. Those half reactions were

$$\underbrace{Zn \rightarrow Zn^{2+} + 2e^-}_{\text{aanode}}$$

$$\underbrace{2H^+ + 2e^- \rightarrow H_2}_{\text{cathode}}$$

The propensity of zinc to oxidize coupled with that of hydrogen to reduce creates a potential energy difference between the electrodes at which these processes occur. And like any potential energy difference, it can create a force which can be used to do work. In this case, the work is that of pushing electrons through a circuit. The work of such a process can be calculated by integrating

$$dw_e - -E\,dQ$$

where E is the potential energy difference, and dQ is an infinitesimal amount of charge carried through the circuit. The infinitesimal amount of charge carried through the circuit can be expressed as

$$dQ = e\,dN$$

where e is the charge carried on one electron ($1.6 \times 10^{-19} C$) and dN is the infinitesimal change in the number of electrons. Thus, if the potential energy difference is constant

$$w_e = -e\,E \int_o^N dN = -N\,e\,E$$

But since the number of electrons carried through a circuit is an enormous number, it would be far more convenient to express this in terms of the number of moles of electrons carried through the circuit. Noting that the number of moles (n) is given by

$$n = \frac{N}{N_A}$$

and that the charge carried by one mole of electrons is given by

$$F = N_A e = 96484\,C$$

where F is **Faraday's constant** and has the magnitude of one Faraday (or the total charge carried by one mole of electrons.) The Faraday is named after Michael Faraday (1791-1867) (Doc, 2014), a British physicist who is credited with inventing the electric motor, among other accomplishments.

Putting the pieces together, the total electrical work accomplished by pushing n moles of electrons through a circuit with a potential difference E, is

$$w_e = -nFE$$

8.5: The connection to ΔG

Recall that in addition to being used as a criterion for spontaneity, ΔG also indicated the maximum amount of non p-V work a system could produce at constant temperature and pressure. And since w_e is non p-V work, it seems like a natural fit that

$$\Delta G = -nFE$$

If all of the reactants and products in the electrochemical cell are in their standard states, it follows that

$$\Delta G^o = -nFE^o$$

where E^o is the **standard cell potential**. Noting that the molar Gibbs function change can be expressed in terms of the reaction quotient Q by

$$\Delta G = \Delta G^o + RT \ln Q$$

it follows that

$$-nFE = -nFE^o + RT \ln Q$$

Dividing by $-nF$ yields

$$E = E^o - \frac{RT}{nF} \ln Q$$

which is the **Nernst equation**. This relationship allows one to calculate the cell potential of a electrochemical cell as a function of the specific activities of the reactants and products. In the Nernst equation, n is the number of electrons transferred per reaction equivalent. For the specific reaction harnessed by Volta in his original battery, E^o = 0.763 V (at 25 °C) and $n = 2$. So if the Zn^{2+} and H^+ ions are at a concentration that gives them unit activity, and the H_2 gas is at a partial pressure that gives it unit fugacity:

$$E = 0.763\,V - \frac{RT}{nF} \ln(1) = 0/763$$

8.6: Half Cells and Standard Reduction Potentials

Much like G itself, E can only be measured as a *difference*, so a convention is used to set a zero to the scale. Toward this end, convention sets the reduction potential of the standard hydrogen electrode (SHE) to 0.00 V.

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-$$

wtih $E^o_{ox} = 0.763\,V$

$$2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \rightarrow \mathrm{H}_2$$

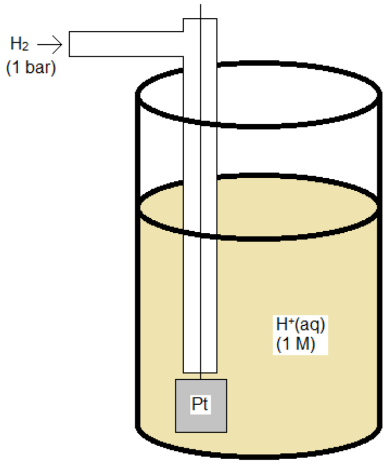
with $E^o_{red} = 0.000\,V$

Standard Hydrogen Electrode

The standard hydrogen electrode is constructed so that H_2 gas flows over an inert electrode made of platinum, and can interact with an acid solution which provides H^+ for the half reaction

$$2\,\mathrm{H}^+(\mathrm{aq}) + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2(\mathrm{g})$$

Both H^+ and H_2 need to have unit activity (or fugacity), which if the solution and gas behave ideally means a concentration of 1 M and a pressure of 1 bar.



Electrochemical Cells

Standard reduction potentials can be measured relative to the convention of setting the reduction potential of the **Standard Hydrogen Electrode** (SHE) to zero. A number of values are shown in Table P1.

✓ Example 8.6.1: Cell Potential and Spontaneity

Which pair of reactants will produce a spontaneous reaction if everything is present in its standard state at 25 °C?

- Fe and Cu^{2+} or
- Fe^{2+} and Cu

Solution

The species with the standard reduction potential (Table P1) will force the other to oxidize.

From the table,

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Cu}$$

with $0.337\,V$

$$\mathrm{Fe}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Fe}$$

with $-0.440\,V$

So the iron half-reaction will flip (so that iron is oxidizing) and the spontaneous reaction under standard conditions will be

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$$

with $E^o = 0.777\,V$

Calculating Cell Potentials

Using values measured relative to the SHE, it is fairly easy to calculate the standard cell potential of a given reaction. For example, consider the reaction

$$2\,\mathrm{Ag^+(aq)} + \mathrm{Cu(s)} \rightarrow 2\,\mathrm{Ag(s)} + \mathrm{Cu^{2\,+}(aq)}$$

Before calculating the cell potential, we should review a few definitions. The anode half reaction, which is defined by the half-reaction in which oxidation °Ccurs, is

$$\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2\,+}(aq)} + 2\,\mathrm{e^-}$$

And the cathode half-reaction, defined as the half-reaction in which reduction takes place, is

$$\mathrm{Ag^+(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}$$

Using **standard cell notation**, the conditions (such as the concentrations of the ions in solution) can be represented. In the standard cell notation, the anode is on the left-hand side, and the cathode on the right. The two are typically separated by a **salt bridge**, which is designated by a double vertical line. A single vertical line indicates a phase boundary. Hence for the reaction above, if the silver ions are at a concentration of 0.500 M, and the copper (II) ions are at a concentration of 0.100 M, the standard cell notation would be

✓ Example 8.6.2: Cell Potential Under nonstadard Conditions

Calculate the cell potential at 25 °C for the cell indicated by

$$\mathrm{Cu(s)|Cu^{2\,+}(aq,\ 0\cdot 100\ M)||Ag^+(aq,\ 0\cdot 500\ M)|Ag(s)}$$

Solution

In order to calculate the cell potential (E), the standard cell potential must first be obtained. The standard cell potential at 25 °C is given by

$$\begin{aligned} E_{cell} &= E^o_{cathode} - E^o_{anode} \\ &= 0.799\,V - 0.337\,V \\ &= 0.462\,V \end{aligned}$$

And for a cell at non-standard conditions, such as those indicated above, the Nernst equation can be used to calculate the cell potential. At 25 °C, The cell potential is given by

$$\begin{aligned} E_{cell} &= E^o_{cell} - \frac{RT}{nF}\ln\left(\frac{[Cu^{2+}]}{[Ag^+]}\right) \\ &= 0.462\,V - \frac{(8.314\,J/(mol\,K)(298\,K)}{2(96484\,C)}\ln\left(\frac{0.100\,M}{0.500\,M}\right) \end{aligned}$$

Noting that $1\,J/C = 1\,V$,

$$E = 0.483\,V$$

✓ Example 8.6.3: Cell Potential under Non-Standard Conditions

Calculate the cell potential at 25 °C for the cell defined by

$$Ni(s)|Ni^{2+}(aq,\ 0.500\ M)||Cu(s)|Cu^{2+}(aq,\ 0.100\ M)$$

Solution

We will use the Nernst equation. First, we need to determine E^o. Using Table P1, it is apparent that

$$\mathrm{Cu^{2}\,^{+}2\,e^{-} \rightarrow Cu}$$

$E^o = 0.337\,V$

$$\mathrm{Ni^{2\,+} + 2\,e^{-} \rightarrow Ni}$$

with $E^o = -0.250\,V$

So copper, having the larger reduction potential will be the cathode half-reaction while forcing nickel to oxidize, making it the anode. So E^o for the cell will be given by

$$E_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= 0.337\,V - (-0.250\,V)$$

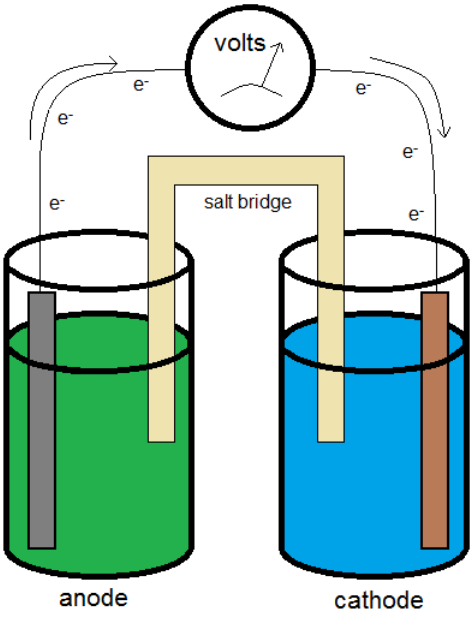
$$= 0.587\,V$$

And the cell potential is then given by the Nernst Equation

$$\begin{aligned} E_{cell} &= E^o_{cell} - \frac{RT}{nF}\ln Q \\ &= 0.587 - \frac{(8.314\,J/(mol\,K)(298\,K)}{2(96484\,C)}\ln\left(\frac{0.500\,M}{0.100\,M}\right) \\ &= 0.566\,V \end{aligned}$$

Measuring the Voltage

A typical galvanic electrochemical cell can be constructed similar to what is shown in the diagram above. The electrons flow from the anode (the electron source) to the cathode (the electron sink.) The salt bridge allows for the flow of ions to complete the circuit while minimizing the introduction of a junction potential.



8.7: Entropy of Electrochemical Cells

The Gibbs function is related to entropy through its temperature dependence

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

A similar relationship can be derived for the temperature variance of E^o.

$$nF\left(\frac{\partial E^o}{\partial T}\right)_p = \Delta S \tag{8.7.1}$$

Consider the following data for the Daniel cell (Buckbeei, Surdzial, & Metz, 1969) which is defined by the following reaction

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

T (°C)	0	10	20	25	30	40
Eo (V)	1.1028	1.0971	1.0929	1.0913	1.0901	1.0887

From a fit of the data to a quadratic function, the temperature dependence of

$$\left(\frac{\partial E^o}{\partial T}\right)_p$$

is easily established.

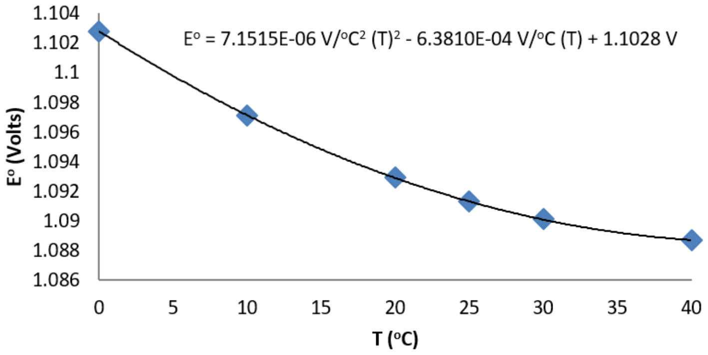


Figure 8.7.1: Temperature dependence of the cell potential for a Daniel cell.

The quadratic fit to the data results in

$$\left(\frac{\partial E^o}{\partial T}\right)_p = 3.8576 \times 10^{-6} \frac{V}{^\circ C^2}(T) - 6.3810 \times 10^{-4} \frac{V}{^\circ C}$$

So, at 25 °C,

$$\left(\frac{\partial E^o}{\partial T}\right)_p = -54166 \times 10^{-4} V/K$$

noting that K can be substituted for $^\circ C$ since in difference they have the same magnitude. So the entropy change is calculated (Equation 8.7.1) is

$$\Delta S = nF\left(\frac{\partial E^o}{\partial T}\right)_p = (2\, mol)(95484\, C/mol)(-5.4166 \times 10^{-4} V/K)$$

Because

$$1\, C \times 1\, V = 1\, J$$

The standard entropy change for the Daniel cell reaction at 25 °C is

$$\Delta S = -104.5\, J/(mol\, K).$$

It is the negative entropy change that leads to an increase in standard cell potential at lower temperatures. For a reaction such as

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$$

which has a large increase in entropy (due to the production of a gas-phase product), the standard cell potential decreases with decreasing temperature. As this is the reaction used in most car batteries, it explains why it can be difficult to start ones car on a very cold winter morning. The topic of temperature dependence of several standard cell potentials is reported and discussed by Bratsch (Bratsch, 1989).

8.8: The Nernst Equation

The standard cell potential $E^\circ_{\text{cell, eq}}$ of a cell reaction is the equilibrium cell potential of the hypothetical galvanic cell in which each reactant and product of the cell reaction is in its standard state and there is no liquid junction potential. The value of $E^\circ_{\text{cell, eq}}$ for a given cell reaction with given choices of standard states is a function only of temperature. The measured equilibrium cell potential $E_{\text{cell, eq}}$ of an actual cell, however, depends on the activities of the reactants and products as well as on temperature and the liquid junction potential, if present.

To derive a relation between $E_{\text{cell, eq}}$ and activities for a cell without liquid junction, or with a liquid junction of negligible liquid junction potential, we substitute expressions for $\Delta_r G$ and for $\Delta_r G^\circ$ from Eqs. 14.3.13 and Eq. 14.3.15 into $\Delta_r G = \Delta_r G^\circ + RT \ln Q_{\text{rxn}}$ (Eq. 11.8.8) and solve for $E_{\text{cell, eq}}$:

$$E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - \frac{RT}{zF} \ln Q_{\text{rxn}} \tag{14.4.1}$$

(no liquid junction, or E_{j}=0)

Equation 14.4.1 is the **Nernst equation** for the cell reaction. Here Q_{rxn} is the reaction quotient for the cell reaction defined by Eq. 11.8.6: $Q_{\text{rxn}} = \prod_i a_i^{\nu_i}$.

The rest of this section will assume that the cell reaction takes place in a cell without liquid junction, or in one in which E_{j} is negligible.

If each reactant and product of the cell reaction is in its standard state, then each activity is unity and $\ln Q_{\text{rxn}}$ is zero. We can see from the Nernst equation that the equilibrium cell potential $E_{\text{cell, eq}}$ in this case has its standard value $E^\circ_{\text{cell, eq}}$, as expected. A decrease in product activities or an increase in reactant activities decreases the value of $\ln Q_{\text{rxn}}$ and increases $E_{\text{cell, eq}}$, as we would expect since $E_{\text{cell, eq}}$ should be greater when the forward cell reaction has a greater tendency for spontaneity.

If the cell reaction comes to reaction equilibrium, as it will if we short-circuit the cell terminals with an external wire, the value of Q_{rxn} becomes equal to the thermodynamic equilibrium constant K, and the Nernst equation becomes $E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - (RT/zF) \ln K$. The term $(RT/zF) \ln K$ is equal to $E^\circ_{\text{cell, eq}}$ (Eq. 14.3.16), so $E_{\text{cell, eq}}$ becomes zero—the cell is “dead” and is incapable of performing electrical work on the surroundings.

At T=298.15 K(25.00 °C), the value of RT/F is 0.02569 V, and we can write the Nernst equation in the compact form

$$E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - \frac{0.02569\ \text{V}}{z} \ln Q_{\text{rxn}} \tag{14.4.2}$$

(T=298.15 K)

As an illustration of an application of the Nernst equation, consider the reaction equation

$$\text{H}_2(\text{g}) + 2\,\text{AgCl}(\text{s}) \rightarrow 2\,\text{H}^+(\text{aq}) + 2\,\text{Cl}^-(\text{aq}) + 2\,\text{Ag}(\text{s}) \tag{8.8.1}$$

This reaction takes place in a cell without liquid junction (Fig. 14.1), and the electrolyte solution can be aqueous HCl. The expression for the reaction quotient is

$$Q_{\text{rxn}} = \frac{a_+^2 a_-^2 a_{\text{Ag}}^2}{a_{\text{H}_2} a_{\text{AgCl}}^2} \tag{14.4.3}$$

We may usually with negligible error approximate the pressure factors of the solids and solutes by unity. The activities of the solids are then 1, the solute activities are $a_+ = \gamma_+ m_+/m^\circ$ and $a_- = \gamma_- m_-/m^\circ$, and the hydrogen activity is $a_{\text{H}_2} = f_{\text{H}_2}/p^\circ$. The ion molalities m_+ and m_- are equal to the HCl molality m_{B}. The expression for Q_{rxn} becomes

$$Q_{\text{rxn}} = \frac{\gamma_+^2 \gamma_-^2 (m_{\text{B}}/m^\circ)^4}{f_{\text{H}_2}/p^\circ} = \frac{\gamma_\pm^4 (m_{\text{B}}/m^\circ)^4}{f_{\text{H}_2}/p^\circ} \tag{14.4.4}$$

and the Nernst equation for this cell is

$$\begin{aligned} E_{\text{cell, eq}} &= E^\circ_{\text{cell, eq}} - \frac{RT}{2F} \ln \frac{\gamma_\pm^4 (m_{\text{B}}/m^\circ)^4}{f_{\text{H}_2}/p^\circ} \\ &= E^\circ_{\text{cell, eq}} - \frac{2RT}{F} \ln \gamma_\pm - \frac{2RT}{F} \ln \frac{m_{\text{B}}}{m^\circ} + \frac{RT}{2F} \ln \frac{f_{\text{H}_2}}{p^\circ} \end{aligned} \tag{14.4.5}$$

By measuring $E_{\text{cell, eq}}$ for a cell with known values of m_{B} and f_{H_2}, and with a derived value of $E^{\circ}_{\text{cell, eq}}$, we can use this equation to find the mean ionic activity coefficient $\gamma_{\pm}$ of the HCl solute. This is how the experimental curve for aqueous HCl in Fig. 10.3 was obtained.

> We can always multiply each of the stoichiometric coefficients of a reaction equation by the same positive constant without changing the meaning of the reaction. How does this affect the Nernst equation for the reaction equation above? Suppose we decide to multiply the stoichiometric coefficients by one-half:
>
> $$\frac{1}{2}\text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}(\text{s})$$
>
> With this changed reaction equation, the value of z is changed from 2 to 1 and the Nernst equation becomes
>
> $$E_{\text{cell, eq}} = E^{\circ}_{\text{cell, eq}} - \frac{RT}{F}\ln\frac{\gamma_{\pm}^2 (m_{\text{B}}/m^{\circ})^2}{(f_{\text{H}_2}/p^{\circ})^{1/2}} \tag{14.4.6}$$
>
> which yields the same value of $E_{\text{cell, eq}}$ for given cell conditions as Eq. 14.4.5. This value must of course be unchanged, because physically the cell is the same no matter how we write its cell reaction, and measurable physical quantities such as $E_{\text{cell, eq}}$ are unaffected. However, molar reaction quantities such as $\Delta_{\text{r}}G$ and $\Delta_{\text{r}}G^{\circ}$ *do* depend on how we write the cell reaction, because they are changes per extent of reaction.

8.9: Evaluation of the Standard Cell Potential

As we have seen, the value of the standard cell potential $E^\circ_{\text{cell, eq}}$ of a cell reaction has useful thermodynamic applications. The value of $E^\circ_{\text{cell, eq}}$ for a given cell reaction depends only on temperature. To evaluate it, we can extrapolate an appropriate function to infinite dilution where ionic activity coefficients are unity.

To see how this procedure works, consider again the cell reaction $\mathrm{H_2(g) + 2\,AgCl(s) \rightarrow 2\,H^+(aq) + 2\,Cl^-(aq) + 2\,Ag(s)}$. The cell potential depends on the molality m_{B} of the HCl solute according to Eq. 14.4.5. We can rearrange the equation to

$$E^\circ_{\text{cell, eq}} = E_{\text{cell, eq}} + \frac{2RT}{F}\ln\gamma_\pm + \frac{2RT}{F}\ln\frac{m_{\text{B}}}{m^\circ} - \frac{RT}{2F}\ln\frac{f_{\text{H}_2}}{p^\circ} \tag{14.5.1}$$

For given conditions of the cell, we can measure all quantities on the right side of Eq. 14.5.1 except the mean ionic activity coefficient $\gamma_\pm$ of the electrolyte. We cannot know the exact value of $\ln\gamma_\pm$ for any given molality until we have evaluated $E^\circ_{\text{cell, eq}}$. We do know that as m_{B} approaches zero, $\gamma_\pm$ approaches unity and $\ln\gamma_\pm$ must approach zero. The Debye–Hückel formula of Eq. 10.4.7 is a theoretical expression for $\ln\gamma_\pm$ that more closely approximates the actual value the lower is the ionic strength. Accordingly, we define the quantity

$$E'_{\text{cell}} = E_{\text{cell, eq}} + \frac{2RT}{F}\left(-\frac{A\sqrt{m_{\text{B}}}}{1+Ba\sqrt{m_{\text{B}}}}\right) + \frac{2RT}{F}\ln\frac{m_{\text{B}}}{m^\circ} - \frac{RT}{2F}\ln\frac{f_{\text{H}_2}}{p^\circ} \tag{14.5.2}$$

The expression in parentheses is the Debye–Hückel formula for $\ln\gamma_\pm$ with I_m replaced by m_{B}. The constants A and B have known values at any temperature (Sec. 10.4), and a is an ion-size parameter for which we can choose a reasonable value. At a given temperature, we can evaluate E'_{cell} experimentally as a function of m_{B}.

The expression on the right side of Eq. 14.5.1 differs from that of Eq. 14.5.2 by contributions to $(2RT/F)\ln\gamma_\pm$ not accounted for by the Debye–Hückel formula. Since these contributions approach zero in the limit of infinite dilution, the extrapolation of measured values of E'_{cell} to m_{B}=0 yields the value of $E^\circ_{\text{cell, eq}}$.

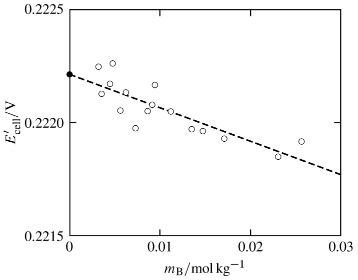


Figure 14.5 E'_{cell} (defined by Eq. 14.5.2) as a function of HCl molality for the cell of Fig. 14.1 at $298.15\,\text{K}$ Data from Herbert S. Harned and Russell W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350–1357, 1932, with f_{H_2} set equal to p_{H_2} and the parameter a set equal to 4.3×10^{-10} m. The dashed line is a least-squares fit to a linear relation.

Figure 14.5 shows this extrapolation using data from the literature. The extrapolated value indicated by the filled circle is $E^\circ_{\text{cell, eq}} = 0.2222$ V, and the uncertainty is on the order of only 0.1 mV.

- **14.5: Evaluation of the Standard Cell Potential** by Howard DeVoe is licensed CC BY 4.0. Original source: https://www2.chem.umd.edu/thermobook.

CHAPTER OVERVIEW

9: Chemical Kinetics

9.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

9.1.1: The Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 9.1.1:

Under a certain set of conditions, the rate of the reaction

$$\mathrm{N_2 + 3\,H_2 \rightarrow 2\,NH_3}$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution:

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\ M/s$$

$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\ M/s$$

$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\ M/s$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

9.1.2: The Rate Law

As shown above, the rate of the reaction can be followed experimentally by measuring the rate of the loss of a reactant or the rate of the production of a product. The rate of the reaction is often related to the concentration of some or all of the chemical species present at a given time. An equation called the *rate law* is used to show this relationship. The rate law **cannot** be predicted by looking at the balanced chemical reaction but must be determined by experiment. For example, the rate law for the reaction

$$\mathrm{Cl_2(g) + CO(g) \rightarrow Cl_2CO(g)}$$

was experimentally determined to be

$$\text{rate} = k[Cl_2]^{3/2}[CO]$$

In this equation, k is the rate constant, and $[\mathrm{Cl_2}]$ and $[\mathrm{CO}]$ are the molar concentrations of Cl_2 and of CO. Each exponent is called the *order* of the given species. Thus, the rate law is second order in Cl_2 and first order in CO. The sum of the individual reactant orders is called the **reaction order**. This reaction has a reaction order of two and a half.

In the next section, we will discuss methods to experimentally determine the rate law.

9.1.3: Contributors and Attributions

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)
- Tom Neils (Grand Rapids Community College)

9.2: The Method of Initial Rates

The **method of initial rates** is a commonly used technique for deriving rate laws. As the name implies, the method involves measuring the initial rate of a reaction. The measurement is repeated for several sets of initial concentration conditions to see how the reaction rate varies. This might be accomplished by determining the time needed to exhaust a particular amount of a reactant (preferably one on which the reaction rate does not depend!) A typical set of data for a reaction

$$A + B \rightarrow products$$

might appear as follows:

Run	[A] (M)	[B] (M)	Rate (M/s)
1	0.0100	0.0100	0.0347
2	0.0200	0.0100	0.0694
3	0.0200	0.0200	0.2776

The analysis of this data involves taking the ratios of rates measured where one of the concentrations does not change. For example, assuming a rate law of the form

$$\text{rate} = k[A]^\alpha [B]^\beta \tag{9.2.1}$$

The ratio of runs i and j generate the following relationship.

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[A]_i^\alpha [B]_i^\beta}{k[A]_j^\alpha [B]_j^\beta}$$

So using runs 1 and 2,

$$\frac{0.0347\,M/s}{0.0694\,M/s} = \frac{\cancel{k}(0.01\,M/s)^\alpha\ \cancel{(0.01\,M/s)^\beta}}{\cancel{k}(0.02\,M/s)^\alpha\ \cancel{(0.01\,M/s)^\beta}}$$

this simplifies to

$$\frac{1}{2} = \left(\frac{1}{2}\right)^\alpha$$

So clearly, \(\alpha = 1\) and the reaction is 1st order in A. Taking the ratio using runs 2 and 3 yields

$$\frac{0.0694\,M/s}{0.2776\,M/s} = \frac{\cancel{k}(0.02\,M)^\alpha\ \cancel{(0.01\,M)^\beta}}{\cancel{k}(0.02\,M)^\alpha\ \cancel{(0.02\,M)^\beta}}$$

This simplifies to

$$\frac{1}{4} = \left(\frac{1}{2}\right)^\beta \tag{9.2.2}$$

By inspection, one can conclude that \(\beta = 2\), and that the reaction is second order in B. But if it is not so clear (as it might not be if the concentration is not incremented by a factor of 2), the value of \(\beta\) can be determined by taking the natural logarithm of both sides of the Equation 9.2.2.

$$\begin{aligned} \ln \frac{1}{4} &= \ln \left(\frac{1}{2}\right)^\beta \\ &= \beta \ln \left(\frac{1}{2}\right) \end{aligned}$$

dividing both sides by $\ln(1/2)$

$$\frac{\ln\left(\frac{1}{4}\right)}{\ln\left(\frac{1}{2}\right)} = \beta \frac{\ln\left(\frac{1}{2}\right)}{\ln\left(\frac{1}{2}\right)}$$

or

$$\beta = \frac{-1.3863}{-0.69315} = 2$$

And so the rate law (Equation 9.2.1) can be expressed as

$$\text{rate} = k[A][B]^2$$

And is 1st order in A, 2nd order in B, and 3rd order overall. The rate constant can then be evaluated by substituting one of the runs into the rate law (or using all of the data and taking an average). Arbitrarily selecting the first run for this,

$$0.0347\ M/s = k(0.01\ M/s)(0.01\ M/s)^2$$

This results in a value of k

$$k = \frac{0.0347\ M/s}{(0.01\ M/s)(0.01\ M/s)^2} = 3.47 \times 10^5\ M^{-2} s^{-1}$$

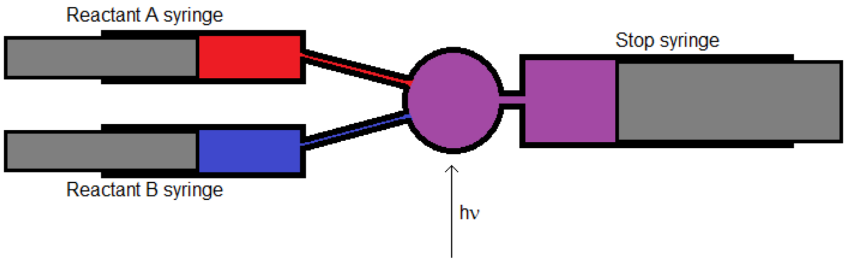
It is useful to note that the units on k are consistent with a 3rd order rate law.

9.3: Rate Laws Must Be Determined Experimentally

There are several methods that can be used to measure chemical reactions rates. A common method is to use spectrophotometry to monitor the concentration of a species that will absorb light. If it is possible, it is preferable to measure the appearance of a product rather than the disappearance of a reactant, due to the low background interference of the measurement. However, high-quality kinetic data can be obtained either way.

9.3.1: The Stopped-Flow Method

The **stopped-flow method** involves using flow control (which can be provided by syringes or other valves) to control the flow of reactants into a mixing chamber where the reaction takes place. The reaction mixture can then be probed spectrophotometrically. Stopped-flow methods are commonly used in physical chemistry laboratory courses (Progodich, 2014).



Some methods depend on measuring the initial rate of a reaction, which can be subject to a great deal of experimental uncertainty due to fluctuations in instrumentation or conditions. Other methods require a broad range of time and concentration data. These methods tend to produce more reliable results as they can make use of the broad range of data to smooth over random fluctuations that may affect measurements. Both approaches (initial rates and full concentration profile data methods) will be discussed below.

9.4: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \tag{9.4.1}$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is ln[A]$_0$.

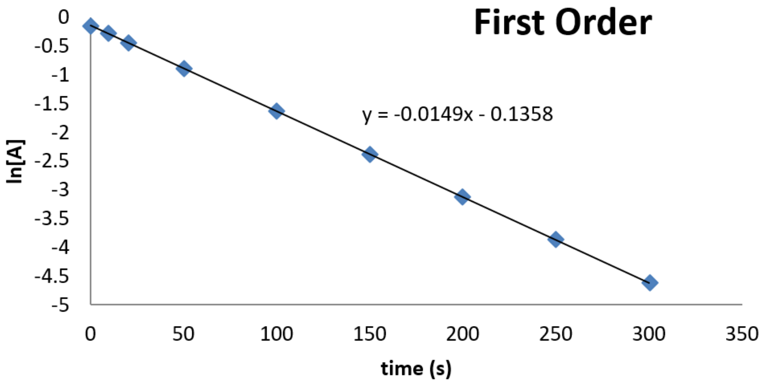
✓ Example 9.4.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation 9.4.1) can be expressed in exponential form:

$$[A] = [A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

9.5: Different Rate Laws Predict Different Kinetics

Difference rate laws predict different kinetics

9.5.1: Zero-order Kinetics

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt} = k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A] = -k\int_{t_o}^{t} dt$$

which yields

$$[A] - [A]_o = -kt$$

or

$$[A] = [A]_o - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0th order kinetics. If they are not, other possibilities must be considered.

9.5.2: Second Order Kinetics

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{9.5.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{9.5.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 9.5.2 is

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

or

$$\frac{1}{[A]}=\frac{1}{[A]_o}+kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2$^{\text{nd}}$ order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A+B\rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt}=k[A][B]$$

and

$$-\frac{d[B]}{dt}=k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A]=[A]_o-[P] \tag{9.5.3}$$

and

$$[B]=[B]_o-[P] \tag{9.5.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt}=k[A][B] \tag{9.5.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 9.5.3 and 9.5.4) into the rate law expression (Equation 9.5.5) yields

$$\frac{d[P]}{dt}=k([A]_o-[P])([B]=[B]_o-[P]) \tag{9.5.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o-[P])([B]=[B]_o-[P])}=k\,dt$$

Noting that at time $t=0$, $[P]=0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]}\frac{d[P]}{([A]_o-[P])([B]_o-[P])}=\int_{t=0}^{t}k\,dt$$

Consulting a table of integrals reveals that for $a\neq b$ [1],

$$\int\frac{dx}{(a-x)(b-x)}=\frac{1}{b-a}\ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0\neq[B]_0$) results in

$$\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B]_0-[P]}{[A]_0-[P]}\right)\Bigg|_0^{[A]}=k\,t|_0^t$$

$$\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B]_0-[P]}{[A]_0-[P]}\right)-\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right)=k\,t \tag{9.5.7}$$

Substituting Equations 9.5.3 and 9.5.4 into Equation 9.5.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right)=kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m=([B]_0-[A]_0)k.$$

In the limit at $[A]_0=[B]_0$, then $[A]=[B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate}=k[A]^2$$

and integrate direct like in Equation 9.5.1 and the integrated rate law is (as before)

$$\frac{1}{[A]}=\frac{1}{[A]_o}+kt$$

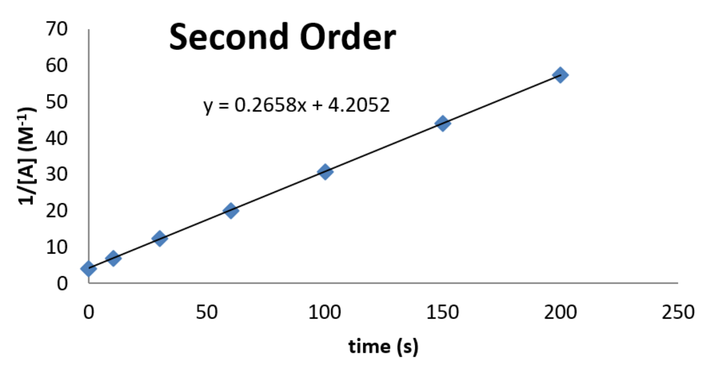
Example 9.5.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t=0$ can also be inferred from the intercept.

---

[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

Example 9.5.3

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

$$2N_2O_5\,(soln)\rightarrow 4NO_2\,(soln)+O_2\,(g)$$

This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	−3.310	27.4
600	0.0274	−3.597	36.5

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
1200	0.0206	−3.882	48.5
1800	0.0157	−4.154	63.7
2400	0.0117	−4.448	85.5
3000	0.00860	−4.756	116
3600	0.00640	−5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

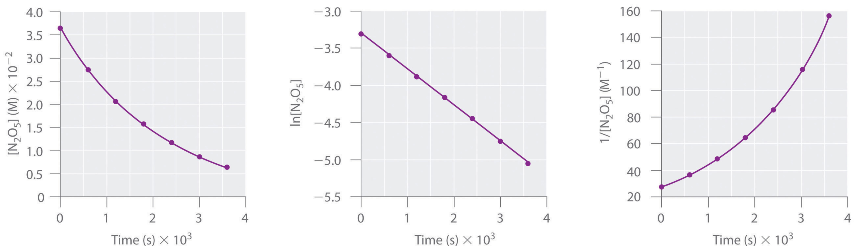
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 13.4.2 to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[N_2O_5]$ versus t, $\ln[N_2O_5]$ versus t, and $1/[N_2O_5]$ versus t:



The plot of $\ln[N_2O_5]$ versus t gives a straight line, whereas the plots of $[N_2O_5]$ versus t and $1/[N_2O_5]$ versus t do not. This means that the decomposition of N_2O_5 is first order in $[N_2O_5]$.

B The rate law for the reaction is therefore

$$rate = k\,[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus t for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[N_2O_5]$ versus t. Using the points for $t = 0$ and 3000 s,

$$slope = \frac{ln[N_2O_5]_{3000} - ln[N_2O_5]_0}{3000\ s - 0\ s} = \frac{[-4.756] - [-3.310]}{3000\ s} = 4.820 \times 10^{-4}\ s^{-1}$$

Thus $k = 4.820 \times 10^{-4}\ s^{-1}$.

9.5.3: Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

9.6: The Method of Half-Lives

Another method for determining the order of a reaction is to examine the behavior of the **half-life** as the reaction progresses. The half-life can be defined as the time it takes for the concentration of a reactant to fall to half of its original value. The method of half-lives involved measuring the half-life's dependence on concentration. The expected behavior can be predicted using the integrated rate laws we derived earlier.

Using the definition of the half-life, at time $t_{1/2}$ the concentration $[A]$ drops to half of its original value, $[A]_0$.

$$[A] = \frac{1}{2}[A]_o$$

at $t = t_{1/2}$.

So if the reaction is 0th order in A, after one half-life

$$\frac{1}{2}[A]_o = [A]_o - kt_{1/2}$$

Solving for $t_{1/2}$ reveals the dependence of the half-life on the initial concentration.

$$\frac{[A]_o}{2k} = t_{1/2}$$

So as the original concentration is **decreased**, the half-life of a 0th order reaction will also **decrease**.

Similarly, for a first order reaction,

$$\frac{1}{2}[A]_o = [A]_o e^{-kt_{1/2}}$$

and solving for $t_{1/2}$ results in a concentration independent expression

$$\frac{\ln 2}{k} = t_{1/2}$$

It is because the half-life of a 1st order reaction is **independent** of concentration that it is oftentimes used to describe the rate of first order processes (such as radioactive decay.)

For a 2nd order reaction, the half-life can be expressed based on the integrated rate law.

$$\frac{1}{\frac{1}{2}[A]_o} = \frac{1}{[A]_o} + kt_{1/2}$$

solving for $t_{1/2}$ yields

$$\frac{1}{t_{1/2}} = t_{1/2}$$

In the case of a second order reaction, the half-life **increases** with **decreasing** initial concentration.

Table 9.6.1: Calculated half lives for Reactions following simple Rate Laws

Order	Half-life	Behavior
0th	$\frac{1}{2}[A]_o = [A]_o - kt_{1/2}$	Decreases as the reaction progresses (as [A] decreases
1st	$[\frac{\ln 2}{k} = t_{1/2}$	Remains constant as the reaction progresses (is independent of concentration)
2nd	$\frac{1}{\frac{1}{2}[A]_o} = \frac{1}{[A]_o} + kt_{1/2}$	Increases with decreasing concentration.

For reactions in which the rate law depends on the concentration of more than one species, the half-life can take a much more complex form that may depend on the initial concentrations of multiple reactants, or for that matter, products!

✓ Example 9.6.1: Radiocarbon Dating

Carbon-14 decays into nitrogen-14 with first order kinetics and with a half-life of 5730 years.

$$^{14}\text{C} \rightarrow {}^{14}\text{N}$$

What is the rate constant for the decay process? What percentage of carbon-14 will remain after a biological sample has stopped ingesting carbon-14 for 1482 years?

Solution

The rate constant is fairly easy to calculate:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{5730\, yr} = 1.21 \times 10^{-4}\, yr^{-1}$$

Now the integrated rate law can be used to solve the second part of the problem.

$$[^{14}\text{C}] = [^{14}\text{C}]_o e^{-kt}$$

this can be rewritten in term of relative loss of $[^{14}\text{C}]$.

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_o} = e^{-kt}$$

so

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_o} = e^{-(1.21\times 10^{-4}\, yr^{-1})(1482\, ys)} = 0.836$$

So after 1482 years, there is 83.6 % of ^{14}C still left.

✓ Example 9.6.2:

Based on the following concentration data as a function of time, determine the behavior of the half-life as the reaction progresses. Use this information to determine if the following reaction is 0th order, 1st order, or 2nd order in A. Also, use the data to estimate the rate constant for the reaction.

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600
30	0.480
40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

Solution

If the original concentration is taken as 1.200 M, half of the original concentration is 0.600 M. The reaction takes 20 seconds to reduce the concentration to half of its original value. If the original concentration is taken as 0.800 M, it clearly takes 30 seconds for the concentration to reach half of that value. Based on this methodology, the following table is easy to generate:

$[A]_o$ (M)	1.200	0.800	0.600	0.400
$t_{1/2}$ (s)	20	30	40	60

The rate constant can be calculated using any of these values:

$$k = \frac{1}{[A]t_{1/2}} \tag{9.6.1}$$

$$= \frac{1}{(0.8\,M)(30\,s)} \tag{9.6.2}$$

$$= 0.0417\,M^{-1}s^{-1} \tag{9.6.3}$$

9.7: Complex Rate Laws

It is essential to specify that the order of a reaction and its molecularity are equal only for elementary reactions. Reactions that follow complex laws are composed of several elementary steps, and they usually have non-integer reaction orders, for at least one of the reactants.

Consecutive reactions

A reaction that happens following a sequence of two elementary steps can be written as follows:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

Assuming that each of the steps follows a first order kinetic law, and that only the reagent A is present at the beginning of the reaction, we can write the differential change in concentration of each species with respect to infinitesimal time dt, using the following formulas:

$$\begin{aligned} -\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}] \Rightarrow [\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t) \\ \frac{d[\mathrm{B}]}{dt} &= k_1[\mathrm{A}] - k_2[\mathrm{B}] \\ \frac{d[\mathrm{C}]}{dt} &= k_2[\mathrm{B}]. \end{aligned} \tag{9.7.1}$$

These three equations represent a system of differential equations with three unknown variables. Unfortunately, these equations are linearly dependent on each other, and they are not sufficient to solve the system for each variable. To do so, we need to include a fourth equation, coming from the conservation of mass:

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]. \tag{9.7.2}$$

Using the first equation in Equation 9.7.1, we can now replace the concentration $[\mathrm{A}]$ in the second equation and solve for $[\mathrm{B}]$:

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = k_1[\mathrm{A}]_0 \exp(-k_1 t), \tag{9.7.3}$$

which can be simplified by multiplying both sides by $\exp(k_2 t)$:

$$\begin{aligned} \left(\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}]\right)\exp(k_2 t) &= k_1[\mathrm{A}]_0 \exp[(k_2 - k_1)t] \\ \Rightarrow \frac{d\left\{[\mathrm{B}]\exp(k_2 t)\right\}}{dt} &= k_1[\mathrm{A}]_0 \exp[(k_2 - k_1)t], \end{aligned} \tag{9.7.4}$$

which can then be integrated remembering that $[B]_0 = 0$, and $\int \exp(kx) = \dfrac{1}{k}\exp(kx)$:

$$[\mathrm{B}] = \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0[\exp(-k_1 t) - \exp(-k_2 t)]. \tag{9.7.5}$$

We can then use both $[\mathrm{A}]$, from Equation 9.7.1, and $[\mathrm{B}]$, from Equation 9.7.5, in Equation 9.7.2 to solve for $[\mathrm{C}]$:

$$\begin{aligned} [\mathrm{C}] &= [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}] \\ &= [\mathrm{A}]_0 - [\mathrm{A}]_0 \exp(-k_1 t) - \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0[\exp(-k_1 t) - \exp(-k_2 t)] \\ &= [\mathrm{A}]_0 \left\{1 + \frac{-k_2 \exp(-k_1 t) + k_1 \exp(-k_2 t)}{k_2 - k_1}\right\}. \end{aligned} \tag{9.7.6}$$

From these results, we can distinguish two extreme behaviors. The first one is observed when $k_1 \cong k_2$, and it produces a plot of the concentration of species with respect to time reported in Figure 9.7.1. This behavior is observed when a process undergoing a series of consecutive reactions present a rate-determining step in the middle of the sequence (the second reaction, in the simple case analyzed above). Once the process is established, its rate will equate the rate of the slowest step.

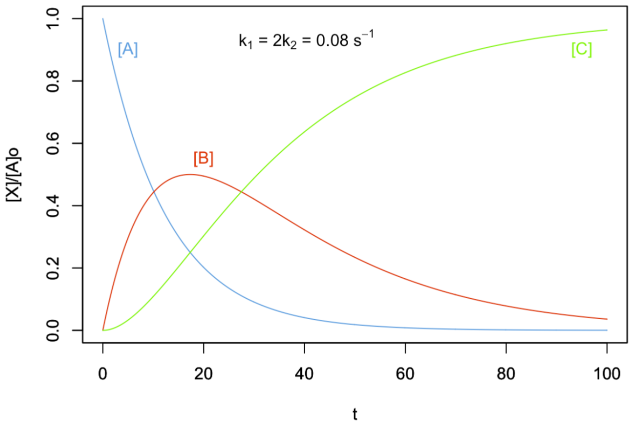


Figure 9.7.1: Concentration Plot for a Process with Two Consecutive Reactions with the Second One Being the Rate-Determining Step.

The second behavior is observed when $k_1 \ll k_2$, and it produces the plot in Figure 9.7.2 In this case, the concentration of the intermediate species B is not relevant throughout the process, and the rate-determining step is the first reaction. As such, the process has the same rate law as an elementary reaction going directly from A to C.

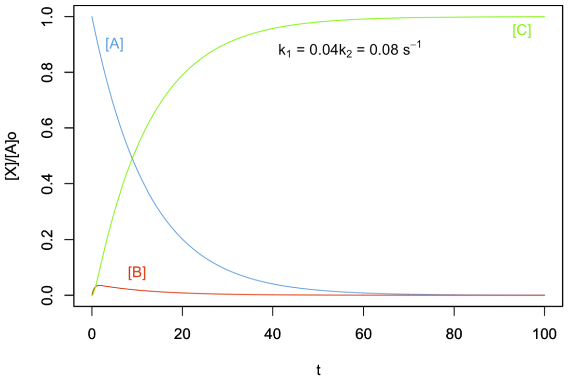


Figure 9.7.2: Concentration Plot for a Process with Two Consecutive Reactions with the First One Being the Rate-Determining Step.

Since the concentration of B is small and relatively constant throughout the process, $\frac{d[\mathrm{B}]}{dT} = 0$. We can then simplify the mathematical treatment of these reactions by eliminating it from the process altogether. This simplification is known as the *steady-state approximation*. It is used in chemical kinetics to study processes that undergo a series of reactions producing intermediate species whose concentrations are constants throughout the entire process.

$$\begin{gathered} \mathrm{A} \xrightarrow{k_1} \mathrm{I}_1 \xrightarrow{k_2} \mathrm{I}_2 \longrightarrow \cdots \xrightarrow{k_n} \text{products} \\ \text{Steady State Approximation:} \\ \mathrm{A} \xrightarrow{\hspace{6cm}} \text{products} \end{gathered} \tag{9.7.7}$$

Competitive reactions

A process where two elementary reactions happen in parallel, competing with each can be written as follows:

$$\begin{tikzcd} & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$

Assuming that each step follows first order kinetic, we can write:

$$
\begin{aligned}
-\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}]+k_2[\mathrm{A}] \Rightarrow [\mathrm{A}]=[\mathrm{A}]_0\exp[-(k_1+k_2)t] \\
\frac{d[\mathrm{B}]}{dt} &= k_1[\mathrm{A}] \Rightarrow [\mathrm{B}]=\frac{k_1}{k_1+k_2}[\mathrm{A}]_0\{1-\exp[-(k_1+k_2)t]\} \\
\frac{d[\mathrm{C}]}{dt} &= k_2[\mathrm{A}] \Rightarrow [\mathrm{C}]=\frac{k_2}{k_1+k_2}[\mathrm{A}]_0\{1-\exp[-(k_1+k_2)t]\}\,.
\end{aligned}
$$

The concentration of each of the species can then be plotted against time, obtaining the diagram reported in Figure 9.7.3. The final concentrations of the products, $[\mathrm{B}]_f$ and $[\mathrm{C}]_f$, will depend on the values of the two rate coefficients. For example, if $k_1>k_2$, $[\mathrm{B}]_f>[\mathrm{C}]_f$, as in Figure 9.7.3, but if $k_1<k_2$, $[\mathrm{B}]_f<[\mathrm{C}]_f$.

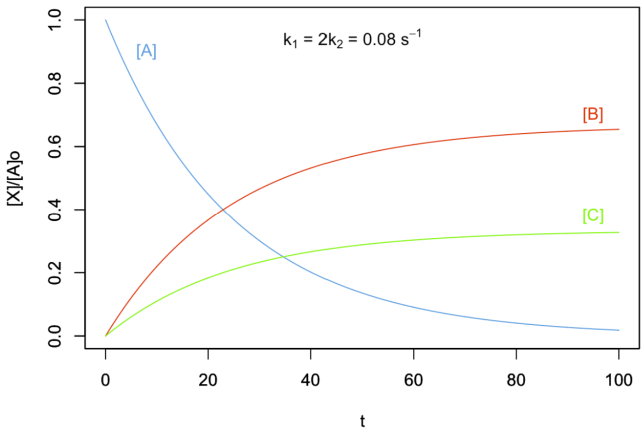


Figure 9.7.3: Concentration Plot for a Process with Two Competitive Reactions.

An important relationship that can be derived from Equation 9.7.1 is that:

$$\frac{[\mathrm{B}]}{[\mathrm{C}]}=\frac{k_1}{k_2}.$$

Opposed reactions

Another case of complex kinetic law happens when a pair of forward and reverse reactions occur simultaneously:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

where the rate coefficients for the forward and backwards reaction, k_1 and k_{-1} respectively, are not necessarily equal to each other, but comparable in magnitude. We can write the rate laws for each of these elementary steps as:

$$
\begin{aligned}
-\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}]-k_{-1}[\mathrm{B}]=k_1[\mathrm{A}]-k_{-1}([\mathrm{A}]_0-[\mathrm{A}]) \\
\frac{d[\mathrm{A}]}{dt} &= -(k_1+k_{-1})[\mathrm{A}]+k_{-1}[\mathrm{A}]_0,
\end{aligned}
\tag{9.7.8}
$$

which can then be integrated to:

$$
\begin{aligned}
[\mathrm{A}] &= [\mathrm{A}]_0\frac{k_{-1}+k_1\exp[-(k_1+k_{-1})t]}{k_1+k_{-1}} \\
[\mathrm{B}] &= [\mathrm{A}]_0\left\{1-\frac{k_{-1}+k_1\exp[-(k_1+k_{-1})t]}{k_1+k_{-1}}\right\}.
\end{aligned}
\tag{9.7.9}
$$

These formulas can then be used to obtain the plots in Figure 9.7.4.

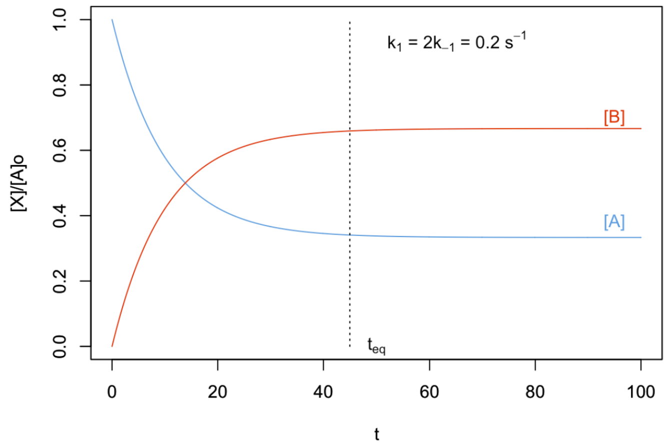


Figure 9.7.4: Concentration Plot for a Process with Two Opposed Reactions.

As can be seen from the plots in Figure $9.7.4$, after a sufficiently long time, the systems reach a dynamic equilibrium, where the concentration of A and B don’t change. These equilibrium concentrations can be calculated replacing $t=\infty$ in Equation 9.7.8:

$$\begin{aligned}[\mathrm{A}]_{\mathrm{eq}} &= [\mathrm{A}]_0\frac{k_{-1}}{k_1+k_{-1}} \\ [\mathrm{B}]_{\mathrm{eq}} &= [\mathrm{A}]_0\frac{k_1}{k_1+k_{-1}}.\end{aligned} \tag{9.7.10}$$

Considering that the concentrations of the species don’t change at equilibrium:

$$\begin{aligned}-\frac{d[\mathrm{A}]_{\mathrm{eq}}}{dt} &= \frac{d[\mathrm{B}]_{\mathrm{eq}}}{dt} = 0 \\ &\Rightarrow k_1[\mathrm{A}]_{\mathrm{eq}} = k_{-1}[\mathrm{B}]_{\mathrm{eq}} \\ &\Rightarrow \frac{k_1}{k_{-1}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_C,\end{aligned} \tag{9.7.11}$$

where K_C is the equilibrium constant as defined in chapter 10. This is a rare link between kinetics and thermodynamics and appears only for opposed reactions after sufficient time has passed so that the system can reach the dynamic equilibrium.

- **15.2: Complex Rate Laws** by Roberto Peverati is licensed CC BY-SA 4.0. Original source: https://peverati.github.io/pchem1/.

9.8: Reaction Mechanisms

A **reaction mechanism** is a set of **elementary reactions** steps, that when taken in aggregate define a chemical pathway that connects reactants to products. An elementary reaction is one that proceeds by a single process, such a molecular (or atomic) decomposition or a molecular collision. Typically, elementary reactions only come in **unimolecular**

$$A \rightarrow products$$

and **bimolecular**

$$A + B \rightarrow products$$

form. Occasionally, an elementary step that is **termolecular**

$$A + B + C \rightarrow products$$

(involved the simultaneous collision of three atoms or molecules) but it is generally a pair of bimolecular steps acting in rapid succession, the first forming an activated complex, and the second stabilizing that complex chemically or physically.

$$A + B \rightarrow AB^*$$

$$AB^* + C \rightarrow AB + C^*$$

The wonderful property of elementary reactions is that the **molecularity** defines the order of the rate law for the reaction step.

The Requirements of a Reaction Mechanism

A valid reaction mechanism must satisfy three important criteria:

1. The sum of the steps must yield the overall stoichiometry of the reaction.
2. The mechanism must be consistent with the observed kinetics for the overall reaction.
3. The mechanism must account for the possibility of any observed side products formed in the reaction.

Example 9.8.1:

For the reaction

$$A + B \rightarrow C$$

is the following proposed mechanism valid?

$$A + A \xrightarrow{k_1} A_2$$

$$A_2 + B \xrightarrow{k_1} C + A$$

Solution

Adding both proposed reactions gives

$$\cancel{2}A + \cancel{A_2} + B \rightarrow \cancel{A_2} + C + \cancel{A}$$

Canceling those species that appear on both sides of the arrow leaves

$$A + B \rightarrow C$$

which is the reaction, so the mechanism is at least stoichiometrically valid. However, it would still have to be consistent with the observed kinetics for the reaction and account for any side-products that are observed.

9.9: The Connection between Reaction Mechanisms and Reaction Rate Laws

The great value of chemical kinetics is that it can give us insights into the actual reaction pathways (mechanisms) that reactants take to form the products of reactions. Analyzing a reaction mechanism to determine the type of rate law that is consistent (or not consistent) with the specific mechanism can give us significant insight. For example, the reaction

$$A + B \rightarrow C$$

might be proposed to follow one of two mechanistic pathways:

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{step 1}}$$

$$\underbrace{A_2 + B \xrightarrow{k_2} C}_{\text{step 2}}$$

or

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{step 1}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{step 2}}$$

The first rate law will predict that the reaction should be second order in A, whereas the second mechanism predicts that it should be first order in A (in the limit that the steady state approximation, discussed in the following sections, can be applied to A_2 and A^*). Based on the observed rate law being first or second order in A, one can rule out one of the rate laws. Unfortunately, this kind of analysis cannot confirm a specific mechanism. Other evidence is needed to draw such conclusions, such as the spectroscopic observation of a particular reaction intermediate that can only be formed by a specific mechanism.

In order analyze mechanisms and predict rate laws, we need to build a toolbox of methods and techniques that are useful in certain limits. The next few sections will discuss this kind of analysis, specifically focusing on

- the **Rate Determining Step** approximation,
- the **Steady State** approximation, and
- the **Equilibrium** approximation.

Each type of approximation is important in certain limits, and they are oftentimes used in conjunction with one another to predict the final forms of rate laws.

9.10: The Rate Determining Step Approximation

The **rate determining step** approximation is one of the simplest approximations one can make to analyze a proposed mechanism to deduce the rate law it predicts. Simply stated, the rate determining step approximation says that a mechanism can proceed no faster than its slowest step. So, for example, if the reaction

$$A + B \rightarrow C$$

is proposed to follow the mechanism

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{slow}}$$

$$\underbrace{A_2 \xrightarrow{k_2} C + A}_{\text{fast}}$$

the rate determining step approximation suggests that the rate (expressed in terms of the appearance of product C) should be determined by the slow initial step, and so the rate law will be

$$\frac{[C]}{dt} = k_1[A]^2$$

matching the order of the rate law to the molecularity of the slow step. Conversely, if the reaction mechanism is proposed as

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{slow}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{fast}}$$

the rate determining step approximation suggests that the rate of the reaction should be

$$\frac{[C]}{dt} = k_1[A]$$

again, with the order of the rate law matching the molecularity of the rate determining step.

9.11: The Steady-State Approximation

One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction

$$A + B \rightarrow C \tag{9.11.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{9.11.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{9.11.3}$$

The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B] \approx 0$$

or

$$[A_2] \approx \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

the above expression for $[A_2]$ can be substituted

$$\frac{d[C]}{dt} = k_2\left(\frac{k_1[A]^2}{k_2[B]}\right)[B]$$

of

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$.

Alternatively, if the mechanism for Equation 9.11.1 is proposed to be

$$A \xrightarrow{k_1} A^* \tag{9.11.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{9.11.5}$$

then the rate of change of the concentration of A^* is

$$\frac{[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds, then

$$[A^*] \approx \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\begin{aligned}\frac{d[C]}{dt} &= k_2[A^*][B] \qquad (9.11.6)\\ &= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\,\cancel{[B]}}\right)\cancel{[B]} \qquad (9.11.7)\end{aligned}$$

or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

9.12: The Equilibrium Approximation

In many cases, the formation of a reactive intermediate (or even a longer lived intermediate) involves a reversible step. This is the case if the intermediate can decompose to reform reactants with a significant probability as well as moving on to form products. In many cases, this will lead to a pre-equilibrium condition in which the **equilibrium approximation** can be applied. An example of a reaction mechanism of this sort is

$$A+B \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} AB$$

$$AB \xrightarrow{k_2} C$$

Given this mechanism, the application of the steady state approximation is cumbersome. However, if the initial step is assumed to achieve equilibrium, an expression can be found for $[AB]$. In order to derive this expression, one assumes that the rate of the forward reaction is equal to the rate of the reverse reaction for the initial step in the mechanism.

$$k_1[A][B] = k_{-1}[AB]$$

or

$$\frac{k_1[A][B]}{k_{-1}} = [AB]$$

This expression can be substituted into an expression for the rate of formation of the product C:

$$\frac{d[C]}{dt} = k_2[AB]$$

or

$$\frac{d[C]}{dt} = \frac{k_2k_1}{k_{-1}}[A][B]$$

Which predicts a reaction rate law that is first order in A, first order in B, and second order overall.

✓ Example 9.12.1:

Given the following mechanism, apply the equilibrium approximation to the first step to predict the rate law suggested by the mechanism.

$$A+A \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} A_2$$

$$A_2+B \xrightarrow{k_2} C+A$$

Solution

If the equilibrium approximation is valid for the first step,

$$k_1[A]^2 = k_{-1}[A_2]$$

or

$$\frac{k_1[A]^2}{k_{-1}} \approx [A_2]$$

Plugging this into the rate equation for the second step

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

yields

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}}[A]^2[B]$$

Thus, the rate law has the form

$$\text{rate} = k'[A]^2[B]$$

which is second order in A, first order in B and third order over all, and in which the effective rate constant (k' is

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

Sometimes, the equilibrium approximation can suggest rate laws that have negative orders with respect to certain species. For example, consider the following reaction

$$A + 2B \rightarrow 2C$$

A proposed mechanism for which might be

$$A + B \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} I + C$$

$$I + B \xrightarrow{k_2} C$$

in which I is an intermediate. Applying the equilibrium approximation to the first step yields

$$k_1[A][B] = k_{-1}[I][C]$$

or

$$\frac{k_1[A][B]}{k_{-1}[C]} \approx [I]$$

Substituting this into an expression for the rate of formation of C, one sees

$$\frac{d[C]}{dt} = k_2[I][B]$$

or

$$\frac{d[C]}{dt} = \frac{k_1[A][B]}{k_{-1}[C]}[B] = \frac{k_2 k_1[A][B]}{k_{-1}[C]}$$

The rate law is then of the form

$$\text{rate} = k\frac{[A][B]^2}{[C]}$$

which is first order in A, second order in B, negative one order in C, and second order overall. Also,

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

In this case, the negative order in C means that a buildup of compound C will cause the reaction to slow. These sort of rate laws are not uncommon for reactions with a reversible initial step that forms some of the eventual reaction product.

9.13: Arrhenius Equation

It is common knowledge that chemical reactions occur more rapidly at higher temperatures. Milk turns sour much more rapidly if stored at room temperature rather than in a refrigerator; butter goes rancid more quickly in the summer than in the winter; and eggs hard-boil more quickly at sea level than in the mountains. For the same reason, cold-blooded animals such as reptiles and insects tend to be more lethargic on cold days.

The reason for this is not hard to understand. Thermal energy relates direction to motion at the molecular level. As the temperature rises, molecules move faster and collide more vigorously, greatly increasing the likelihood of bond cleavages and rearrangements. Whether it is through the collision theory, transition state theory, or just common sense, chemical reactions are typically expected to proceed faster at higher temperatures and slower at lower temperatures.

By 1890 it was common knowledge that higher temperatures speed up reactions, often doubling the rate for a 10-degree rise, but the reasons for this were not clear. Finally, in 1899, the Swedish chemist Svante Arrhenius (1859-1927) combined the concepts of activation energy and the Boltzmann distribution law into one of the most important relationships in physical chemistry:

$$k = \underbrace{A}_{\text{pre-exponential factor}} e^{-\frac{\overset{\text{activation energy}}{E_a}}{\underbrace{RT}_{\text{average kinetic energy}}}}$$

Take a moment to focus on the meaning of this equation, neglecting the A factor for the time being. First, note that this is another form of the exponential decay law discussed in the previous section of this series. What is "decaying" here is not the concentration of a reactant as a function of time, but the magnitude of the rate constant as a function of the exponent $–E_a /RT$. And what is the significance of this quantity? Recalling that RT is the *average kinetic energy*, it becomes apparent that the exponent is just the ratio of the activation energy E_a to the average kinetic energy. The larger this ratio, the smaller the rate (hence the negative sign). This means that high temperature and low activation energy favor larger rate constants, and thus speed up the reaction. Because these terms occur in an exponent, their effects on the rate are quite substantial.

The two plots below show the effects of the activation energy (denoted here by $E^‡$) on the rate constant. Even a modest activation energy of 50 kJ/mol reduces the rate by a factor of 10^8.

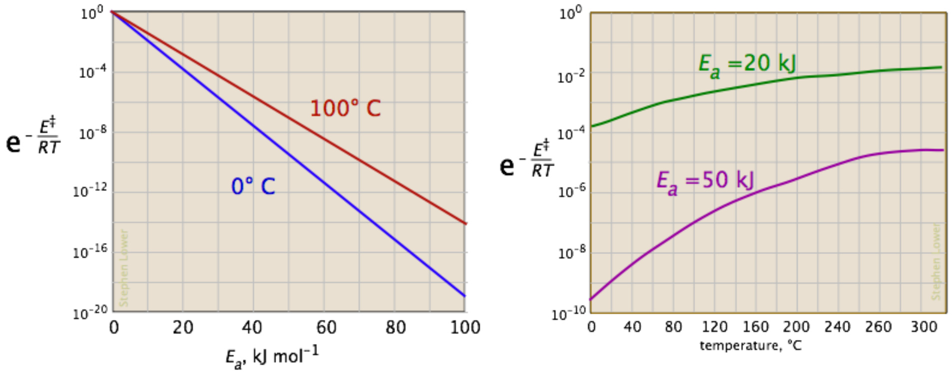


Figure 9.13.1: Arrhenius plots. The logarithmic scale in the right-hand plot leads to nice straight lines.

Looking at the role of temperature, a similar effect is observed. (If the *x*-axis were in "kilodegrees" the slopes would be more comparable in magnitude with those of the kilojoule plot at the above right.)

Determining the Activation Energy

The Arrhenius equation,

$$k = Ae^{-E_a/RT} \tag{9.13.1}$$

can be written in a non-exponential form that is often more convenient to use and to interpret graphically. Taking the logarithms of both sides and separating the exponential and pre-exponential terms yields

$$\ln k = \ln\left(Ae^{-E_a/RT}\right) \tag{9.13.2}$$

$$= \ln A + \ln\left(e^{-E_a/RT}\right) \tag{9.13.3}$$

$$= \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{9.13.4}$$

Equation 9.13.4is in the form of $y = mx + b$ - the equation of a straight line.

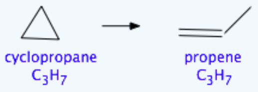
$$\ln k = \ln A - \frac{E_a}{RT}$$

where temperature is the independent variable and the rate constant is the dependent variable. So if one were given a data set of various values of k, the rate constant of a certain chemical reaction at varying temperature T, one could graph $\ln(k)$ versus $1/T$. From the graph, one can then determine the slope of the line and realize that this value is equal to $-E_a/R$. One can then solve for the activation energy by multiplying through by -R, where R is the gas constant.

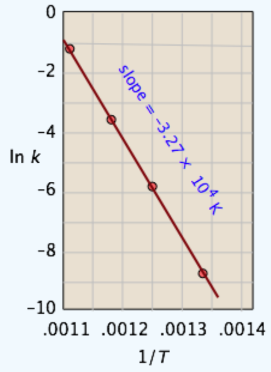
This affords a simple way of determining the activation energy from values of k observed at different temperatures, by plotting $\ln k$ as a function of $1/T$.

✓ Example 9.13.1: Isomerization of Cyclopropane

For the isomerization of cyclopropane to propene,



the following data were obtained (calculated values shaded in pink):



T, °C	477	523	577	623
$1/T$, K^{-1} × 10^3	1.33	1.25	1.18	1.11
k, s^{-1}	0.00018	0.0027	0.030	0.26
ln k	–8.62	–5.92	–3.51	–1.35

From the calculated slope, we have

$$\begin{aligned} -\left(\frac{E_a}{R}\right) &= -3.27 \times 10^4 K \\ E_a &= -(8.314\, J\, mol^{-1} K^{-1})(-3.27 \times 10^4\ K) \\ &= 273\, kJ\, mol^{-1} \end{aligned}$$

Comment: This activation energy is high, which is not surprising because a carbon-carbon bond must be broken in order to open the cyclopropane ring. (C–C bond energies are typically around 350 kJ/mol.) This is why the reaction must be carried out at high temperature.

Calculating E_a without a plot

Because the ln k-vs.-1/T plot yields a straight line, it is often convenient to estimate the activation energy from experiments at only two temperatures. To see how this is done, consider that

$$\begin{aligned} \ln k_2 - \ln k_1 &= \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right) \\ &= \boxed{\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \end{aligned}$$

The ln-A term is eliminated by subtracting the expressions for the two ln-k terms.) Solving the expression on the right for the activation energy yields

$$E_a = \frac{R \ln \frac{k_2}{k_1}}{\frac{1}{T_1} - \frac{1}{T_2}}$$

✓ Example 9.13.2

A widely used rule-of-thumb for the temperature dependence of a reaction rate is that a **ten degree** rise in the temperature approximately doubles the rate. This is not generally true, especially when a strong covalent bond must be broken. For a reaction that does show this behavior, what would the activation energy be?

Solution

Center the ten degree interval at 300 K. Substituting into the above expression yields

$$
\begin{aligned}
E_a &= \frac{(8.314)(\ln 2/1)}{\dfrac{1}{295} - \dfrac{1}{305}} \\
&= \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(0.693)}{0.00339 \text{ K}^{-1} - 0.00328 \text{ K}^{-1}} \\
&= \frac{5.76 \, J \, mol^{-1} K^{-1}}{(0.00011 \, K^{-1}} \\
&= 52,400 \, J \, mol^{-1} = 52.4 \, kJ \, mol^{-1}
\end{aligned}
$$

Example 9.13.3

It takes about 3.0 minutes to cook a hard-boiled egg in Los Angeles, but at the higher altitude of Denver, where water boils at 92°C, the cooking time is 4.5 minutes. Use this information to estimate the activation energy for the coagulation of egg albumin protein.

Solution

The ratio of the rate constants at the elevations of Los Angeles and Denver is 4.5/3.0 = 1.5, and the respective temperatures are 373 K and 365 K. With the subscripts 2 and 1 referring to Los Angeles and Denver respectively:

$$
\begin{aligned}
E_a &= \frac{(8.314)(\ln 1.5)}{\dfrac{1}{365 \text{ K}} - \dfrac{1}{373 \text{ K}}} \\
&= \frac{(8.314)(0.405)}{0.00274 \text{ K}^{-1} - 0.00268 \text{ K}^{-1}} \\
&= \frac{(3.37 \text{ J mol}^{-1} \text{K}^{-1})}{5.87 \times 10^{-5} \text{ K}^{-1}} \\
&= 57,400 \text{ J mol}^{-1} \\
&= 57.4 \text{ kJ mol}^{-1}
\end{aligned}
$$

Comment: This low value seems reasonable because thermal denaturation of proteins primarily involves the disruption of relatively weak hydrogen bonds; no covalent bonds are broken (although disulfide bonds can interfere with this interpretation).

The Pre-exponential Factor

Up to this point, the pre-exponential term, A in the Arrhenius equation (Equation 9.13.1), has been ignored because it is not directly involved in relating temperature and activation energy, which is the main practical use of the equation.

$$k = Ae^{-E_a/RT}$$

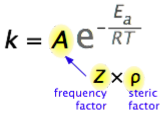
However, because A multiplies the exponential term, its value clearly contributes to the value of the rate constant and thus of the rate. Recall that the exponential part of the Arrhenius equation expresses the fraction of reactant molecules that possess enough kinetic energy to react, as governed by the Maxwell-Boltzmann law. This fraction can run from zero to nearly unity, depending on the magnitudes of E_a and of the temperature.

If this fraction were 0, the Arrhenius law would reduce to

$$k = A$$

In other words, A is the fraction of molecules that would react if either the activation energy were zero, or if the kinetic energy of all molecules exceeded E_a — admittedly, an uncommon scenario (although barrierless reactions have been characterized).

What would limit the rate constant if there were no activation energy requirements? The most obvious factor would be the rate at which reactant molecules come into contact. This can be calculated from kinetic molecular theory and is known as the **frequency-** or **collision factor**, Z.



In some reactions, the relative orientation of the molecules at the point of collision is important, so a geometrical or **steric factor** (commonly denoted by ρ) can be defined. In general, we can express A as the product of these two factors:

$$A = Z\rho$$

Values of ρ are generally very difficult to assess; they are sometime estimated by comparing the observed rate constant with the one in which A is assumed to be the same as Z.

Implications

The exponential term in the Arrhenius equation implies that the rate constant of a reaction increases exponentially when the activation energy decreases. Because the rate of a reaction is directly proportional to the rate constant of a reaction, the rate increases exponentially as well. Because a reaction with a small activation energy does not require much energy to reach the transition state, it should proceed faster than a reaction with a larger activation energy.

In addition, the Arrhenius equation implies that the rate of an uncatalyzed reaction is more affected by temperature than the rate of a catalyzed reaction. This is because the activation energy of an uncatalyzed reaction is greater than the activation energy of the corresponding catalyzed reaction. Since the exponential term includes the activation energy as the numerator and the temperature as the denominator, a smaller activation energy will have less of an impact on the rate constant compared to a larger activation energy. Hence, the rate of an uncatalyzed reaction is more affected by temperature changes than a catalyzed reaction.

The Math in Eliminating the Constant A

To eliminate the constant A, there must be two known temperatures and/or rate constants. With this knowledge, the following equations can be written:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \tag{9.13.5}$$

at T_1 and

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \tag{9.13.6}$$

at T_2. By rewriting Equation 9.13.6:

$$\ln A = \ln k_2 + \frac{E_a}{RT_2} \tag{9.13.7}$$

and substitute for $\ln A$ into Equation 9.13.5:

$$\ln k_1 = \ln k_2 + \frac{E_a}{RT_2} - \frac{E_a}{RT_1} \tag{9.13.8}$$

This simplifies to:

$$\begin{aligned} \ln k_1 - \ln k_2 &= -\frac{E_a}{RT_1} + \frac{E_a}{RT_2} \\ \ln \frac{k_1}{k_2} &= -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \end{aligned}$$

Summary

After observing that many chemical reaction rates depended on the temperature, Arrhenius developed this equation to characterize the temperature-dependent reactions:

$$k = Ae^{\frac{-E_a}{RT}}$$

or

$$\ln k = \ln A - \frac{E_a}{RT}$$

with the following terms:

k: Chemical reaction rate constant

- In unit of s^{-1}(for 1st order rate constant) or M^{-1}s^{-1}(for 2nd order rate constant)

A: The pre-exponential factor or frequency factor

- Specifically relates to molecular collision
- Deals with the frequency of molecules that collide in the correct orientation and with enough energy to initiate a reaction.
- *It is a factor that is determined experimentally, as it varies with different reactions.*
- In unit of L mol^{-1}s^{-1} or M^{-1}s^{-1}(for 2nd order rate constant) and s^{-1}(for 1st order rate constant)
- Because frequency factor A is related to molecular collision, it is temperature dependent
- Hard to extrapolate pre-exponential factor because lnk is only linear over a narrow range of temperature

E_a: The activation energy is the threshold energy that the reactant(s) must acquire before reaching the transition state.

- Once in the transition state, the reaction can go in the forward direction towards product(s), or in the opposite direction towards reactant(s).
- A reaction with a large activation energy requires much more energy to reach the transition state.
- Likewise, a reaction with a small activation energy doesn't require as much energy to reach the transition state.
- In units of J/mol.
- -E$_a$/RT resembles the Boltzmann distribution law.

R: The gas constant.

- Its value is 8.314 J/mol K.

T: The absolute temperature at which the reaction takes place.

- In units of Kelvin (K).

Problems

1. Find the activation energy (in kJ/mol) of the reaction if the rate constant at 600K is 3.4 M^{-1}s^{-1} and 31.0 at 750K.
2. Find the rate constant if the temperature is 289K, Activation Energy is 200kJ/mol and pre-exponential factor is 9 M^{-1}s^{-1}
3. Find the new rate constant at 310K if the rate constant is 7 M^{-1}s^{-1} at 370K, Activation Energy is 900kJ/mol
4. Calculate the activation energy if the pre-exponential factor is 15 M^{-1}s$^{-1,}$ rate constant is 12M^{-1}s^{-1}and it is at 22K
5. Find the new temperature if the rate constant at that temperature is 15M^{-1}s^{-1} while at temperature 389K the rate constant is 7M^{-1}s^{1,} the Activation Energy is 600kJ/mol

Solutions

1. E$_a$ is the factor the question asks to be solved. Therefore it is much simpler to use

$\ln k = -\frac{E_a}{RT} + \ln A$

To find E$_a$, subtract ln A from both sides and multiply by -RT.

This will give us:

$E_a = \ln A - \ln k)RT$

2. Substitute the numbers into the equation:

$lnk = \frac{-(200 \times 1000\ \text{J})}{(8.314\ \text{J mol}^{-1}\text{K}^{-1})(289\ \text{K})} + \ln 9$

$k = 6.37X10^{-36} M^{-1}s^{-1}$

3. Use the equation $ln(k_1/k_2)=-Ea/R(1/T_1-1/T_2)$

$\ln(7/k_2)=-[(900 \text{ X } 1000)/8.314](1/370-1/310)$

$k_2=1.788X10^{-24}\ M^{-1}s^{-1}$

4. Use the equation $k = Ae^{-Ea/RT}$

$12 = 15e^{-Ea/(8.314)(22)}$

$Ea = 40.82J/mol$

5. Use the equatioin $ln(k_1/k_2)=-Ea/R(1/T_1-1/T_2)$

$\ln(15/7)=-[(600 \text{ X } 1000)/8.314](1/T_1 - 1/389)$

$T_1 = 390.6K$

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9.14: The Rate of Bimolecular Gas-Phase Reaction Can Be Estimated Using Hard-Sphere Collision Theory and an Energy-Dependent Reaction Cross Section

9.14.1: **Collision Frequency using the Hard Sphere Model**

For the bimolecular gas-phase reaction

$$\mathrm{Q(g)} + \mathrm{B(g)} \rightarrow \text{products}$$

the reaction rate is

$$\text{rate} = -\frac{d[Q]}{dt} = k[Q][B]$$

If it is assumed that every collision between Q and B particles results in products, the rate at which molecules collide is equal to the frequency of collisions per unit volume, Z_{QB} (Equation 27.6.4)

$$\text{rate} = Z_{QB} = \sigma_{QB}\langle v_r\rangle\rho_Q\rho_B \tag{9.14.1}$$

Also known as the collision frequency, Z_{QB}, has units of molecules per volume per time, molecules·m^{-3}·s^{-1}. It is possible to obtain a rough estimate of the value of the rate constant, k, from the collision frequency.

Equation 9.14.1 shows the rate on a molecular scale. Generally, Z_{QB} is divided by Avogadro's number, N_0, to obtain the collision frequency on a molar scale

$$\text{rate} = -\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = \frac{\sigma_{QB}\langle v_r\rangle}{N_0}\rho_Q\rho_B$$

To convert the number densities to molar concentrations, we need to realize that

$$\frac{\rho_Q}{N_0} = [Q]$$

then

$$-\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = \frac{\sigma_{QB}\langle v_r\rangle}{N_0}(N_0[Q])(N_0[B])$$

$$-\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = N_0\sigma_{QB}\langle v_r\rangle[Q][B]$$

$$-\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = N_0\sigma_{QB}\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}[Q][B]$$

Thus

$$Z_{QB} = N_0^2\sigma_{QB}\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}[Q][B]$$

and

$$k = N_0\sigma_{QB}\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}$$

where:

- $\langle v_r\rangle$ is the mean relative speed of molecules, which is equal to $\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}$
- ρ_Q and ρ_B are the number densities of Q molecules and B molecules
- N$_Q$ and NB are the numbers of Q molecules and B molecules

- σ_{QB} is the averaged sum of the collision cross sections of molecules Q and B, $\sigma_{QB} = \pi \left(\frac{d_Q + d_B}{2} \right)^2$. The collision cross section represents the collision region presented by one molecule to another. σ_{QB} is often written as πd_{QB}^2.

The units of σ are m^2, the units of N_0 are mole^{-1}, and the units of $\langle v_r \rangle$ are $\frac{m}{s}$. Thus, the units of k are $\frac{m^3}{\text{mole} \cdot s}$

As noted earlier, using this hard-sphere collision theory value for the rate constant is a rough estimate, mainly because the temperature dependence of k is improperly represented in the hard-sphere collision theory prediction. The next sections will describe an initial attempt to correct that error.

9.14.2: Successful Collisions

For a successful collision to occur, the reactant molecules must collide with enough kinetic energy to overcome the repulsions of the electron clouds and to break the existing bonds. To take the energy dependence of a successful collision into account, we will introduce a new reaction cross-section, $\sigma_r(v_r)$, which takes into account the speed of the reactants. Thus

$$k(v_r) = v_r \sigma_r(v_r)$$

The rate constant can be calculated by averaging over a distribution of all speeds, $f(v_r)$

$$k = \int_0^\infty k(v_r) f(v_r) dv_r = \int_0^\infty v_r f(v_r) dv_r \sigma_r(v_r) \tag{9.14.2}$$

From equation 27.7.4, we know that $v_r f(v_r) dv_r$ is

$$v_r f(v_r) dv_r = \left(\frac{\mu}{k_B T} \right)^{3/2} \left(\frac{2}{\pi} \right)^{1/2} v_r^3 e^{-\mu v_r^2 / 2 k_B T} dv_r \tag{9.14.3}$$

Equation 9.14.3 presents the rate constant as a function of speed. If we want to compare this version of k with the common, Arrhenius form of k, the dependent variable must be changed from relative speed to relative kinetic energy, E_r. The relationship is

$$E_r = \frac{1}{2} \mu v_r^2 \text{ which rearranges to } v_r = \left(\frac{1}{2 \mu E_r} \right)^{1/2}$$

Thus,

$$dv_r = \left(\frac{1}{2 \mu E_r} \right)^{1/2} dE_r$$

Substituting v_r and dv_r into equation 9.14.3 gives

$$v_r f(v_r) dv_r = \left(\frac{\mu}{k_B T} \right)^{3/2} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{1}{2 \mu E_r} \right)^{3/2} e^{-E_r / k_B T} \left(\frac{1}{2 \mu E_r} \right)^{1/2} dE_r$$

Substituting this equation into equation 9.14.2 and simplifying gives

$$k = \left(\frac{2}{k_B T} \right)^{3/2} \left(\frac{1}{\mu \pi} \right)^{1/2} \int_0^\infty dE_r E_r e^{-E_r / k_B T} \sigma_r(E_r) \tag{9.14.4}$$

We can then assume that the energy dependent reaction cross section $\sigma_r(E_r)$ will include only those molecules which undergo effective collisions with a kinetic energy that is greater than or equal to a minimum sufficient energy, E_0. Thus $\sigma_r(E_r)$ is equal to 0 if $E_r < E_0$ and is equal to σ_{QB} if $E_r \geq E_0$.

Thus,

$$\begin{aligned} k &= \left(\frac{2}{k_B T} \right)^{3/2} \left(\frac{1}{\mu \pi} \right)^{1/2} \int_{E_0}^\infty dE_r E_r e^{-E_r / k_B T} \sigma_{QB} \\ &= \left(\frac{8 k_B T}{\mu \pi} \right)^{1/2} \sigma_{QB} e^{-E_r / k_B T} \left(1 + \frac{E_0}{k_B T} \right) \end{aligned}$$

$$= \langle v_r \rangle \sigma_{QB} e^{-E_r/k_BT} \left(1 + \frac{E_0}{k_BT}\right)$$

This model results in a value for k that takes into account the temperature and a minimum energy requirement to determine the fraction of successful collisions. However, it is not yet equivalent to the Arrhenius equation, in which k is proportional to e^{-E_r/k_BT} and not $e^{-E_r/k_BT}\left(1 + \frac{E_0}{k_BT}\right)$.

9.14.3: References

Atkins, Peter and Julio de Paula. Physical Chemistry for the Life Sciences. 2006. New York, NY: W.H. Freeman and Company.

9.14.4: Contributor

- Tom Neils, Grand Rapids Community College

9.15: A Reaction Cross Section Depends Upon the Impact Parameter

In the previous section, it was assumed that all collisions with sufficient energy would lead to a reaction between the Q and B particles. This is an unrealistic assumption because not all collisions occur with a proper alignment of the particles as shown in Figure $9.15.1$.

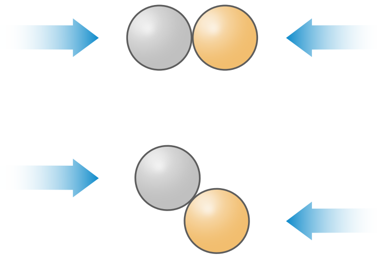


Figure 9.15.1 In the top collision, the particles collide head-on, and thus all of the kinetic energy can be used to overcome electron-electron repulsion and to break bonds. In the bottom collision, the particles collide with a glancing blow so that only part of the kinetic energy is contributed to the reaction process. With collisions involving larger, more complex molecules, there is often a specific molecular orientation required for an effective collision. (CC BY-NC; Ümit Kaya via LibreTexts)

Thus, the energy-dependent reaction cross-section,$\sigma_r(E_r)$, introduced previously is inaccurate and must be modified to take into account the inefficient collisions. One modification is to employ the *line-of-centers* (loc) model for $\sigma_r(E_r)$. This model incorporates the angle of collision relative to the line drawn between the centers of the two colliding particles, as shown in Figure $9.15.2$.

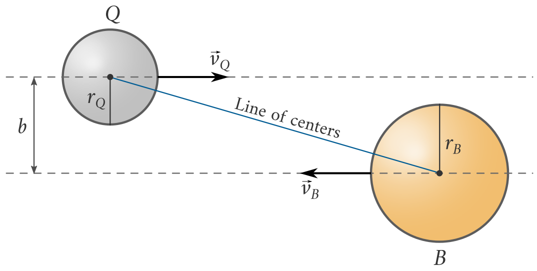


Figure 9.15.2: This figure shows the geometry of the collision between two particles. The particle velocities are $\vec{v}_Q$ and $\vec{v}_B$. The distance between the paths traveled by the two particle centers is b. (CC BY-NC; Ümit Kaya via LibreTexts)

In this model, and effective collision occurs when $E_{loc} > E_0$ where E_{loc} takes into account the fact that all particle collisions are not head-on collisions. If we define v_r as the relative velocity of approach of particles Q and B, then $v_r = \vec{v}_Q - \vec{v}_B$. The relative kinetic energy, E_r, is then $\frac{1}{2}\mu v_r^2$. From Figure $9.15.2$ we can see that the fraction of E_r that can be applied to the collision, (E_{loc}), is dependent upon b, the impact parameter, which is the perpendicular distance between the extrapolated paths traveled by the centers of the particles before the collision occurs. If b is 0, then $E_{loc} = E_r$, but for any other value of b, $E_{loc} < E_r$. If b is greater than the sum of the radii of Q and B, the particles will not collide, and $E_{loc} = 0$. The calculation for determining the exact relationship between the $\sigma_r(E_r)$ and E_r for this line of center model rather complicated, but the result is that $\sigma_r(E_r)$ is equal to 0 if $E_r < E_0$ and is equal to $\sigma_{QB}\left(1 - \frac{E_0}{E_r}\right)$ if $E_r \geq E_0$.

When compared to the simple hard-sphere collision theory, we see that

$$\sigma_r(E_r) = \sigma_{QB} \text{ if } E_r \geq E_0 \text{ (hard-sphere theory)} \tag{9.15.1}$$

$$\sigma_r(E_r) = \sigma_{QB}\left(1 - \frac{E_0}{E_r}\right) \text{ if } E_r \geq E_0 \text{ (line of centers theory)} \tag{9.15.2}$$

If we substitute Equation $9.15.2$ into Equation $30.1.4$ we get

$$\begin{aligned} k &= \left(\frac{2}{k_BT}\right)^{3/2}\left(\frac{1}{\mu\pi}\right)^{1/2}\int_{E_0}^{\infty} dE_r E_r e^{-E_r/k_BT}\sigma_{QB}\left(1-\frac{E_0}{E_r}\right) \\ &= \left(\frac{8k_BT}{\mu\pi}\right)^{1/2}\sigma_{QB}e^{-E_r/k_BT} \\ &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_BT} \end{aligned}$$

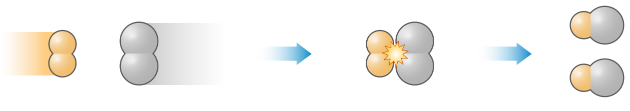
When compared to the simple hard-sphere collision theory, we see that

$$\begin{aligned} k &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_BT}\left(1+\frac{E_0}{k_BT}\right) \text{(hard-sphere theory)} \\ &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_BT} \text{(line of centers theory)} \end{aligned}$$

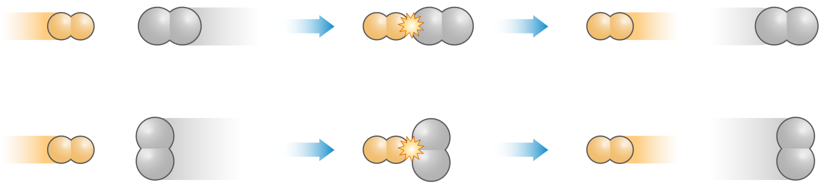
The line of centers theory expresses k in the same terms as the Arrhenius equation, yet experimental values of k still differ from those predicted by the line of centers model. The errors come about because $\sigma_r(E_r)$ is not accurately described by $\sigma_{QB}\left(1-\frac{E_0}{E_r}\right)$. More work needs to be done to improve the model for describing A, the Arrhenius factor.

9.16: The Rate Constant for a Gas-Phase Chemical Reaction May Depend on the Orientations of the Colliding Molecules

In the previous section, the simple hard-sphere model for collisions was modified to take into account the fact that not every collision of particles occurred with sufficient energy to result in a reaction. The line of centers model assumed that all colliding particles were spheres, yet we know that this is definitely not the case. Thus, we need to modify the collision model to factor in the orientation of non-spherical particles. Figure $9.16.1$ shows an example of properly oriented particles and an example of improperly oriented molecules.



Correct orientation



Two of many incorrect orientations

Figure 9.16.1: (top) Molecules colliding with the correct orientation that leads to a successful reaction. (bottom) Molecules colliding in two of the many incorrect orientations that do not lead to a reaction. (CC BY-NC; Ümit Kaya via LibreTexts)

Because proper orientation of colliding molecules is necessary, the hard-sphere collision model overestimates the number of effective collisions. This is one of the factors that leads an incorrect value for A estimated by the hard-sphere collision model.

9.17: Kinetics of Reactions in Solution

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Describe some of the major differences between the kinetics of reactions in the gas phase, compared with those in liquid solutions.
- What role do solvent cages play in solution kinetics?
- Explain the distinction between diffusion-control and activation-control of reaction rates in solutions.
- How can the polarity of a solvent affect the energetics of a reaction mechanism?

The kinetics fundamentals we covered in the earlier sections of this lesson group relate to processes that take place in the gas phase. But chemists and biochemists are generally much more concerned with solutions. This lesson will take you through some of the extensions of basic kinetics that you need in order to understand the major changes that occur when reactions take place in liquid solutions.

What's different about kinetics in liquid solutions?

Most of the added complications of kinetics and rate processes in liquid solutions arise from the *much higher density* of the liquid phase. In a typical gas at atmospheric pressure, the molecules occupy only about 0.2 per cent of the volume; the other 99.8 percent is empty space. In a liquid, molecules may take up more than half the volume, and the "empty" spaces are irregular and ever-changing as the solvent molecules undergo thermal motions of their own.

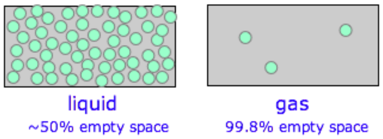


Figure 9.17.1: Liquid vs. Gases.

In a typical liquid solution, the solvent molecules massively outnumber the reactant solute molecules, which tend to find themselves momentarily (~10^{-11} sec) confined to a "hole" within the liquid. This trapping becomes especially important when the solvent is strongly hydrogen-bonded as is the case with water or alcohol.

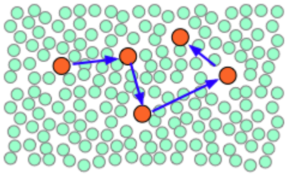
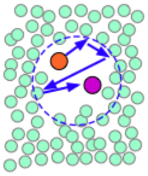
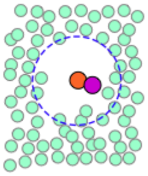
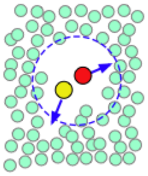
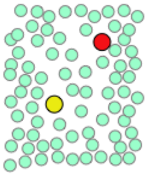


Figure 9.17.2: Brownian motion of a particle in solution

When thermal motions occasionally release a solute molecule from this trap, it will jump to a new location. The jumps are very fast (10^{-12} - 10^{-13} sec) and short (usually a few solvent-molecule diameters), and follow an entirely random pattern, very much as in **Brownian motion**. Consider a simple bimolecular process A + B → products. The reactant molecules will generally be jumping from hole to hole in the solvent matrix, only occasionally finding themselves in the same *solvent cage* where thermal motions are likely to bring them into contact.

Table 9.17.1: Solvent cages and encounter pairs

A pair of reactants end up in the same solvent cage, where they bounce around randomly and exchange kinetic energy with the solvent molecules.	Eventually the two reactants form an *encounter pair*. If they fail to react the first time, they have many more opportunities during the lifetime of the cage.	The products form and begin to move away from each other.	Finally, after about 10^{-11} sec, the solvent cage breaks up and the products diffuse away.

The process can be represented as

$$A + B \rightarrow \{AB\} \rightarrow \text{products} \tag{9.17.1}$$

in which the $\{AB\}$ term represents the caged reactants including the *encounter pair* and the activated complex.

Contrast this scenario with a similar reaction taking place in the gas phase; the molecules involved in the reaction will often be the only ones present, so a significant proportion of the collisions will be A-B encounters. However, if the collision should fail to be energetically or geometrically viable, the reactant molecules fly apart and are unlikely to meet again anytime soon. In a liquid, however, the solute molecules are effectively in a constant state of collision — if not with other reactants, then with solvent molecules which can exchange kinetic energy with the reactants. So once an A-B encounter pair forms, the two reactants get multiple whacks at each other, greatly increasing the probability that they will obtain the kinetic energy needed to kick them over the activation hump before the encounter pair disintegrates.

Limiting Cases: Diffusion-Controlled and Activation-Controlled Reactions

The encounter pair model introduces some new rate parameters:

$$\text{A} + \text{B} \underset{k_{-1}}{\overset{k1}{\rightleftharpoons}} \text{AB} \longrightarrow \text{products} \tag{9.17.2}$$

The first step is an equilibrium between the reactants outside and inside the solvent cage. The rate constants k_1 and k_2 reflect those relating to diffusion of molecules through the solvent; their values are strongly dependent on the viscosity (and thus the temperature) of the solvent. (Note that k_1 is a second-order rate constant, while k_2 is first-order.)

Diffusion is the transport of a substance through a concentration gradient; that is, from a region of higher concentration to one of lower concentration. Think of the way the color of tea spreads out when a tea bag is immersed in hot water. Diffusion occurs because random thermal motions are statistically more likely to move molecules out of a region of higher concentration than in the reverse direction, simply because in the latter case fewer molecules are available to make the reverse trip. Eventually the concentrations become uniform and equilibrium is attained.

As molecules diffuse through a liquid, they must nudge neighboring molecules out of the way. The work required to do this amounts to an activation energy, so diffusion can be thought of as a kinetic process with its own rate constant k_d and activation energy. These parameters depend on the sizes of the solute and solvent molecules and on how strongly the latter interact with each other. This suggests two important *limiting cases* for reactions in solution.

For water at room temperature, k_1 is typically 10^9-10^{10} dm^{-3} mol^{-1} s^{-1} and k_2 is around 10^{-9}-10^{-10} dm^{-3} mol^{-1} s^{-1}. Given these values, $k_3 > 10^{12}$ s^{-1} implies diffusion control, while values $< 10^9$ s^{-1} are indicative of activation control.

- **Diffusion Controlled** ($k_3 \gg k_2$): If the activation energy of the A+B reaction is very small or if escape of molecules from the $\{\text{AB}\}$ cage is difficult, the kinetics will be dominated by k_1, and thus by the activation energy of diffusion. Such a process is said to be *diffusion controlled*. Reactions in aqueous solution in which $E_a > 20$ kJ/mol are likely to fall into this category.
- **Activation Controlled** ($k_3 \ll k_2$): Alternatively, if the activation energy of the A+B reaction dominates the kinetics, and the reaction is *activation-controlled*.

Several general kinds of reactions are consistently very "fast" and thus are commonly found to be diffusion-controlled in most solvents:

Gas-phase rate constants are normally expressed in units of mol s^{-1}, but rate constants of reactions in solution are conventionally given in mol/L units, or dm^3 mol^{-1} s^{-1}. Conversion between them depends on a number of assumptions and is non-trivial.

- **Recombination of atoms and radicals**

For example the formation of I_2 from I atoms in hexane at 298 K has k_3 = 1.3×10^{12} dm^3 mol^{-1} s^{-1}.

- **Acid-base reactions** which involve the transport of H^+ and OH^- ions tend to be very fast.

  The most famous of these is one of the fastest reactions known:

  $$H^+ + OH^- \rightarrow H_2O$$

  for which k_3 = 1.4×10^{11} dm^3 mol^{-1} s^{-1} at 298 K.

Polar solvents such as water and alcohols interact with ions and polar molecules through attractive dipole-dipole and ion-dipole interactions, leading to lower-energy solvated forms which stabilize these species. In this way, a polar solvent can alter both the thermodynamics and kinetics (rate) of a reaction.

Solvent Thermodynamic Effect

If the products of the reaction are markedly more or less polar than the reactants, solvent polarity can change the overal thermodynamics (equilibrium constant) of the reaction. Nowhere is this more apparent than when an ionic solid such as salt dissolves in water. The Na^+ and Cl^- ions are bound together in the solid through strong coulombic forces; pulling the solid apart in a vacuum or in a nonpolar solvent is a highly endothermic process. In contrast, dissolution of NaCl in water is slightly exothermic and proceeds spontaneously.

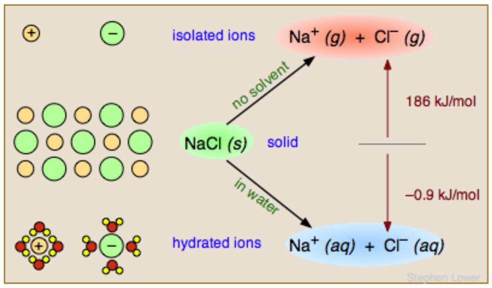
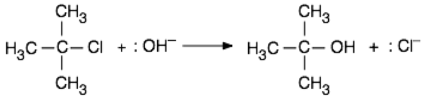


Figure 9.17.3: The solvent thermodynamics effect for table salt in water.

The water facilitates this process in two important ways. First, its high dielectric constant of 80 reduces the force between the separated ions to 1/80 of its normal value. Secondly, the water molecules form a *solvation shell* around the ions (lower left), rendering them energetically (thermodynamically) more stable than they were in the NaCl solid.

Solvent Kinetic Effect

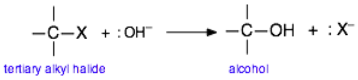
In the same way, a reaction whose mechanism involves the formation of an intermediate or activated complex having a polar or ionic character will have its activation energy, and thus its rate, subject to change as the solvent polarity is altered. As an example we will consider an important class of reactions that you will hear much about if you take a course in organic chemistry. When an aqueous solution of a strong base such as KOH is added to a solution of *tertiary*-butyl chloride in ethanol, the chlorine is replaced by a hydroxyl group, leaving *t*-butyl alcohol as a product:



$$(CH_3)_3C{-}Cl + :OH^- \longrightarrow (CH_3)_3C{-}OH + :Cl^-$$

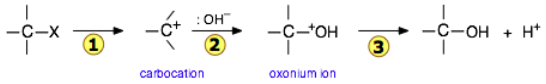
This reaction is one of a large and important class known as *S_N1 nucleophilic substitution processes* that are discussed in most organic chemistry courses. In these reactions, a species that possesses a pair of non-bonding electrons (also called a *nucleophile* or *Lewis base*) uses them to form a new bond with an *electrophile* — a compound in which a carbon atom has a partial positive charge owing to its bonds to electron-withdrawing groups. In the example here, other nucleophiles such as NH_3 or even H_2O would serve as well.

In order to reflect the generality of this process and to focus on the major changes that take place, we will represent this reaction as



$$-\overset{|}{\underset{|}{C}}-X + :OH^- \longrightarrow -\overset{|}{\underset{|}{C}}-OH + :X^-$$

Extensive studies of this class of reactions in the 1930's revealed that it proceeds in two activation energy-controlled steps, followed by a simple dissociation into the products:



In step ①, which is rate-determining, the chlorine leaves the alkyl chloride which becomes an intermediate known as a *carbocation* ("cat-ion"). These ions, in which the central carbon atom lacks a complete octet, are highly reactive, and in step ② the carbocation is attacked by the hydroxide ion which supplies the missing electron. The immediate product is another cation in which the positive charge is on the oxygen atom. This *oxonium ion* is unstable and rapidly dissociates (③)into the alcohol and a hydrogen ion.

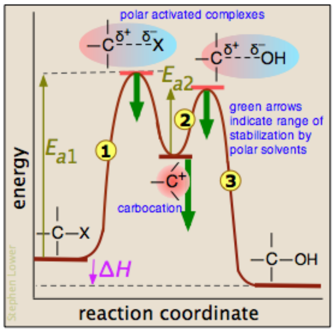


Figure 9.17.4: reaction Coordinate

The reaction coordinate diagram helps us understand the effect of solvent polarity on this reaction. Polar solvent molecules interact most strongly with species in which the electric charge is concentrated in one spot. Thus the carbocation is stabilized to a greater degree than are the activated complexes in which the charge is spread out between the positive and negative ends. As the heavy green arrows indicate, a more polar solvent will stabilize the carbocation more than it will either of the activated complexes; the effect is to materially reduce the activation energy of the rate-determining step, and thus speed up the reaction. Because neither the alkyl chloride nor the alcohol is charged, the change in solvent polarity has no effect on the equilibrium constant of the reaction. This is dramatically illustrated by observing the rate of the reaction in solvents composed of ethanol and water in varying amounts:

Table 9.17.2: Data

% water	10	20	30	40	50	60
$k_1 \times 10^6$	1.7	9.1	40.3	126	367	1294

9.18: Diffusion-controlled Reactions

Diffusion can be described as the random movement of particles through space, usually due to a concentration gradient. Diffusion is a spontaneous process and is a result of the random thermal motions between two particles. The diffusion coefficient (D) can be solved for with Fick's laws of diffusion, which are broken up into two laws.

Fick's First Law of Diffusion

Fick's first law of diffusion is given by the following equation:

$$J = -D\frac{dc}{dx} \tag{9.18.1}$$

where

- J is the flux and is defined by the number or particles that are moving past a given region divided by the area of that region multiplied by the time interval.
- The units of J are mol m^{-2} s^{-1}.
- The letter D represents the diffusion coefficient with units m^2 s and
- c is the concentration of the gradient with units molecules m^{-3}.

Equation 9.18.1 indicates that if the flux and the change in the concentration over time are known, then the diffusion coefficient can be calculated. The negative sign indicates that the concentration gradient is negative. The first law can only be applied to systems in which the conditions remain the same— in other words, if the flux coming into the system equals the flux going out. Fick's second law is more applicable to physical science and other systems that are changing. This second law is applied to systems in which the condition are not steady, or the solution in not equal throughout.

Fick's Second Law of Diffusion

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{9.18.2}$$

Where $\frac{dc}{dt}$ represents the rate of change of concentration in a certain area and $\frac{d^2c}{dx^2}$ represents the changes that the change in concentration can take; this would not be a smooth curve. This term accounts for a varying concentration in the system. If the concentration does not vary, then

$$\frac{d^2c}{dx^2} = 0 \tag{9.18.3}$$

Diffusion can be thought of as a series of random steps that the particle takes as it moves from where it started. These steps can either lead the particle away from where it started, or lead back to where it started. This means that the overall path that a particle takes can look like line overlapping itself multiple times. A third way to calculate the diffusion concentration is through the **Einstein-Smoluchowski equation**:

$$D = \frac{\lambda^2}{2\tau} \tag{9.18.4}$$

where λ is the length that each step takes, and τ is the time that each step takes. In this particular model, each step is the same distance.

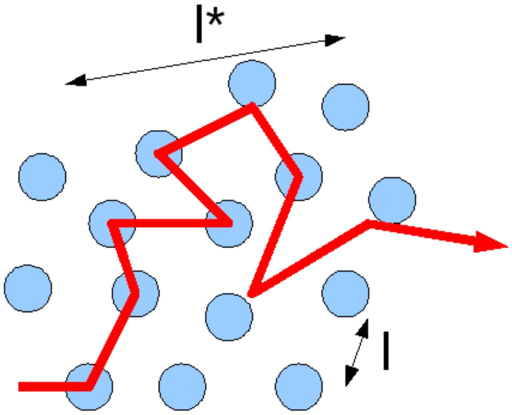


Figure 9.18.1: Scheme showing the mean free path l and the transport length l*. from Wikipedia

The diffusion coefficient is useful because it can tell you something about the system. For example, different substances have different diffusion coefficients, so knowing this can give you an idea of the substance. Ions at room temperature usually have a diffusion coefficient of 0.6×10^{-9} to 2×10^{-9} m^2/s, and biological molecules fall in the range 10^{-11} to 10^{-10} m^2/s. The diffusion coefficient changes as the properties of the system change. For example, at higher temperatures, the diffusion coefficient is greater because the molecules have more thermal motion. The diffusion coefficient is also related to the viscosity of the solution. The greater the diffusion coefficient, the lower the viscosity. Because the rate of diffusion depends on the temperature of the system, the Arrhenius equation can be applied. Applying this equation gives:

$$D = [D]_o e^{-Ea/RT} \tag{9.18.5}$$

The dependence of the diffusion coefficient on the viscosity can be modeled by the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\eta a} \tag{9.18.6}$$

where a is the radius of the molecule and η is the coefficient of viscosity and is defined by:

$$\eta = \eta_o e^{Ea/RT} \tag{9.18.7}$$

This equation demonstrates the dependence of viscosity on temperature.

Contributors and Attributions

- Laura Dickson (UC Davis)

9.19: Diffusion-Limited Reactions

Association Rate

The diffusion-limited association rate is typically approximated from the expression for the relative diffusion of A and B with an effective diffusion constant $D = D_A + D_B$ to within a critical encounter radius $R_0 = R_A + R_B$, as described earlier.

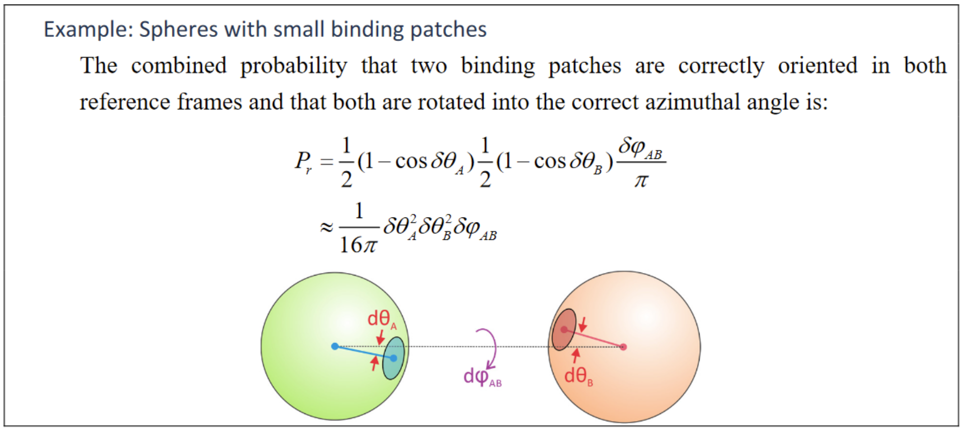
$$k_a = 4\pi R_0 f (D_A + D_B) \tag{9.19.1}$$

One can approximate association rates between two diffusing partners using the Stokes–Einstein expression: $D_A = k_BT/6\pi\eta R_A$. For two identical spheres (i.e., dimerization) in water at T = 300 K, where η ~ 1 cP = 100 kg m^{-1} s^{-1},

$$k_a = \frac{8k_BT}{3\eta} = 6.6 \times 10^9 M^{-1} s^{-1} \tag{9.19.2}$$

Note that this model predicts that the association rate is not dependent on the size or mass of the object.

For bimolecular reactions, the diffusion may also include those orientational factors that bring two binding sites into proximity. Several studies have investigated these geometric effects.



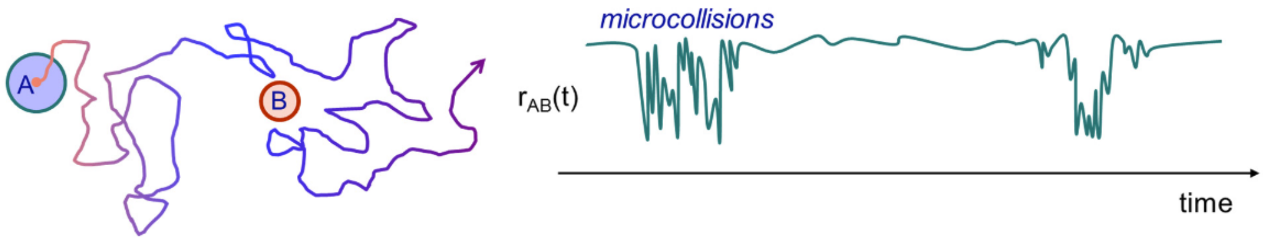
Example: Spheres with small binding patches

The combined probability that two binding patches are correctly oriented in both reference frames and that both are rotated into the correct azimuthal angle is:

$$P_r = \frac{1}{2}(1-\cos\delta\theta_A)\frac{1}{2}(1-\cos\delta\theta_B)\frac{\delta\varphi_{AB}}{\pi}$$

$$\approx \frac{1}{16\pi}\delta\theta_A^2\delta\theta_B^2\delta\varphi_{AB}$$

During diffusive encounter in dilute solution, once two partners collide but do not react, there is a high probability of re-colliding with the same partner before diffusing over a longer range to a new partner. Depending on concentration and the presence of interaction potentials, there may be 5–50 microcollisions with the same partner before encountering a new partner.



Diffusion-Limited Dissociation Rate

For the limit where associations are weak, k_1 and k_{-1} are fast and in equilibrium, and the dissociation is diffusion limited. Then we can calculate k_{-1}

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \tag{9.19.3}$$

Now we consider boundary conditions for flux moving away from a sphere such that

$$C_B(\infty) = 0$$

$$C_B(R_0) = \left(\frac{4}{3}\pi R_0^3\right)^{-1}$$

The boundary condition for concentration at the surface of the sphere is written so that the number density is one molecule per sphere.

The steady state distribution of B is found to be

$$C_B(r) = \frac{3}{4\pi R_0^2 r} \tag{9.19.4}$$

The dissociation flux at the surface is

$$J = -D_B \left(\frac{\partial C_B}{\partial r}\right)_{r=R_0} = \frac{3D_B}{4\pi R_0^4} \tag{9.19.5}$$

and the dissociation frequency is

$$\frac{J}{4\pi R_0^2} = \frac{3D_B}{R_0^2} \tag{9.19.6}$$

When we also consider the dissociative flux for the other partner in the association reaction,

$$k_{-1} = k_d = 3(D_A + D_B)R_0^{-2} \tag{9.19.7}$$

Written in a more general way for a system that may have an interaction potential

$$k_d = \frac{4\pi D e^{U(R_0)/kT}}{\frac{4}{3}\pi R_0^3 \int_{R_0}^{\infty} e^{U(r)kT} r^{-2} dr} = 3DR^* R_0^{-3} \tag{9.19.8}$$

Note that equilibrium constants do not depend on D for diffusion-limited association/dissociation

$$K_D = \frac{k_D}{k_A} = \frac{3DR_0^{-2}}{4\pi R_0 D} = \frac{3}{4\pi R_0^3} \tag{9.19.9}$$

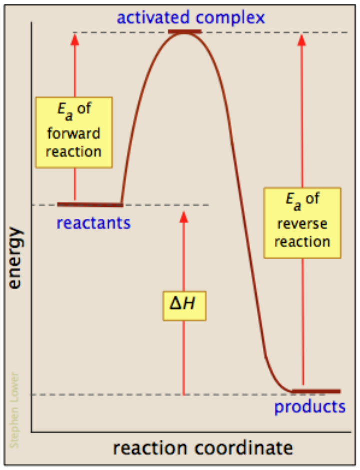
Note this is the inverse of the volume of a sphere.

---

1. D. Shoup, G. Lipari and A. Szabo, Diffusion-controlled bimolecular reaction rates. The effect of rotational diffusion and orientation constraints, Biophys. J. 36 (3), 697-714 (1981); D. Shoup and A. Szabo, Role of diffusion in ligand binding to macromolecules and cell-bound receptors, Biophys. J. 40 (1), 33-39 (1982).

9.17: Basics of Reaction Profiles

Most reactions involving neutral molecules cannot take place at all until they have acquired the energy needed to stretch, bend, or otherwise distort one or more bonds. This critical energy is known as the *activation energy* of the reaction. *Activation energy diagrams* of the kind shown below plot the total energy input to a reaction system as it proceeds from reactants to products.



In examining such diagrams, take special note of the following:

- The "*reaction coordinate*" plotted along the abscissa represents the changes in atomic coordinates as the system progresses from reactants to products. In the very simplest elementary reactions it might correspond to the stretching or twisting of a particular bond, and be shown to a scale. In general, however, the reaction coordinate is a rather abstract concept that cannot be tied to any single measurable and scalable quantity.
- The *activated complex* (also known as the *transition state*) represents the structure of the system as it exists at the peak of the activation energy curve. It does *not* correspond to an identifiable intermediate structure (which would more properly be considered the product of a separate elementary process), but rather to whatever configuration of atoms exists during the collision, which lasts for only about 0.1 picosecond.
- Activation energy diagrams always incorporate the energetics (ΔG or ΔH) of the net reaction, but it is important to understand that the latter quantities depend solely on the thermodynamics of the process which are always independent of the reaction pathway. This means that the same reaction can exhibit different activation energies if it can follow alternative pathways.
- With a few exceptions for very simple processes, activation energy diagrams are largely conceptual constructs based on the standard *collision model* for chemical reactions. It is unwise to read too much into them.

Contributors and Attributions

- Yuliani Sanjaya

9.18: RK3. Activation Barriers

Why do reactions take place at different rates? Why do some happen quickly, and others proceed very slowly? Why might the same reaction proceed at different rates under different conditions? There are a number of factors that influence reaction rates, but this article focuses on the activation barrier.

An activation barrier is a sort of energetic hurdle that a reaction must bypass. Some reactions have higher hurdles and some have lower hurdles. It is easier to overcome lower hurdles, so reactions with low activation barriers can proceed more quickly than ones with higher activation barriers:

- A low activation barrier allows a reaction to happen quickly.
- A high activation barrier makes a reaction proceed more slowly.

A reaction can be exergonic overall, but still have an activation barrier at the beginning. Even if the system decreases in energy by the end of the reaction, it generally experiences an initial increase in energy.

- Even if a reaction gives off energy overall, energy must be added initially to get the reaction started.

This situation is similar to investing in a business. A business generally requires a financial investment to get started. If the business is successful, it will eventually make products and pay money back to the investors. If the business is unable to make back its initial investment, it may fail.

Reactions require an initial investment of energy. This energy may come from surrounding molecules or the environment in general. If the reaction is successful, it will proceed to make products and it will emit energy back to its surroundings.

- It always "costs" a molecule energy to enter into a reaction; it "borrows" that energy from its environment.
- That initial investment of energy may be "paid back" as the reaction proceeds.

All reactions must overcome activation barriers in order to occur. The activation barrier is the sum of the energy that must be expended to get the reaction going. An activation barrier is often pictured as a hill the reactants must climb over during the reaction. Once, there, it can slide down the other side of the hill to become products. At the top of the hill, the molecule exists in what is called the "transition state." At the transition state, the structure is somewhere between its original form and the structure of the products.

RKActivBarrier.png

The type of diagram shown above is sometimes called a "reaction progress diagram." It shows energy changes in the system as a reaction proceeds. One or more activation barriers may exist along the reaction pathways, due to various elementary steps in the reaction.

In order to understand more concretely the terms "reaction progress" and "transition state," consider a real reaction. Suppose a nucleophile, such as an acetylide ion, donates its electrons to an electrophilic carbonyl. The π bond breaks and an alkoxide ion is formed.

RKAlkyneRxn.png

"Reaction progress" refers to how far the reaction has proceeded. The transition state refers specifically to the highest energy point on the pathway from reactants to products. It refers to the structure at that point, and the energy associated with that structure.

In the following diagram, the term "reaction progress" has been replaced by an illustration that matches the status of the reaction with the corresponding point in the energy curve. The structure in the square brackets is the transition state, corresponding to the maximum of the curve. The "double dagger" symbol indicates a transition state structure.

RKAlkyneAddn.png

The transition state is not a true chemical structure. It does not necessarily obey the rules of Lewis structures, because some new bonds have started to form and some old bonds have started to break; partial bonds have no place in a Lewis structure.

Physically, the transition state structure cannot be isolated. Because it sits at the top of an energy curve, the transition state tends to convert into something else. A change in either direction will lower its energy. The tendency is to proceed to lowest energy if possible. As soon as the transition state forms, it will either slide back into the original starting materials or slip forward into the final products.

- The transition state is inherently a high-energy, unstable structure with a very short lifetime. As soon as it is formed, it disappears.

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9.19: Eyring equation

The Eyring Equation, developed by Henry Eyring in 1935, is based on transition state theory and is used to describe the relationship between reaction rate and temperature. It is similar to the Arrhenius Equation, which also describes the temperature dependence of reaction rates. However, whereas Arrhenius Equation can be applied only to gas-phase kinetics, the Eyring Equation is useful in the study of gas, condensed, and mixed-phase reactions that have no relevance to the collision model.

Introduction

The Eyring Equation gives a more accurate calculation of rate constants and provides insight into how a reaction progresses at the molecular level. The Equation is given below:

$$k = \frac{k_B T}{h} e^{-\left(\frac{\triangle H^\ddagger}{RT}\right)} e^{\left(\frac{\triangle S^\ddagger}{R}\right)} \tag{9.19.1}$$

Consider a bimolecular reaction:

$$A + B \rightarrow C \tag{9.19.2}$$

$$K = \frac{[C]}{[A][B]} \tag{9.19.3}$$

where K is the equilibrium constant. In the transition state model, the activated complex AB is formed:

$$A + B \rightleftharpoons AB^\ddagger \rightarrow C \tag{9.19.4}$$

$$K^\ddagger = \frac{[AB]^\ddagger}{[A][B]} \tag{9.19.5}$$

There is an energy barrier, called activation energy, in the reaction pathway. A certain amount of energy is required for the reaction to occur. The transition state, $AB^\ddagger$, is formed at maximum energy. This high-energy complex represents an unstable intermediate. Once the energy barrier is overcome, the reaction is able to proceed and product formation occurs.

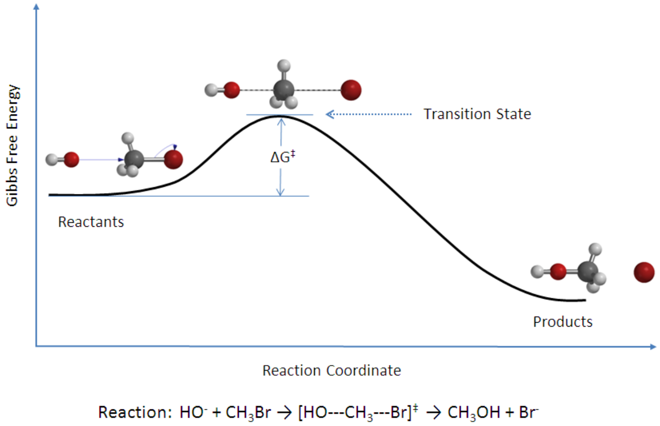


Figure 9.19.1: Reaction coordinate diagram for the bimolecular nucleophilic substitution (S_N2) reaction between bromomethane and the hydroxide anion. form Wikipedia.

The rate of a reaction is equal to the number of activated complexes decomposing to form products. Hence, it is the concentration of the high-energy complex multiplied by the frequency of it surmounting the barrier.

$$\begin{aligned} rate &= v[AB^\ddagger] \qquad (9.19.6) \\ &= v[A][B]K^\ddagger \qquad (9.19.7) \end{aligned}$$

The rate can be rewritten:

$$rate = k[A][B] \tag{9.19.8}$$

Combining Equations 9.19.8 and 9.19.7 gives:

$$k[A][B] = v[A][B]K^{\ddagger} \tag{9.19.9}$$
$$k = vK^{\ddagger} \tag{9.19.10}$$

where

- v is the frequency of vibration,
- k is the rate constant and
- $K^{\ddagger}$ is the thermodynamic equilibrium constant.

The frequency of vibration is given by:

$$v = \frac{k_B T}{h} \tag{9.19.11}$$

where

- k_B is the Boltzmann's constant (1.381 x 10^{-23} J/K),
- T is the absolute temperature in Kelvin (K) and
- h is Planck's constant (6.626 x 10^{-34} Js).

Substituting Equation 9.19.11into Equation 9.19.10:

$$k = \frac{k_B T}{h} K^{\ddagger} \tag{9.19.12}$$

Equation ref is often tagged with another term (M^{1-m}) that makes the units equal with M is the molarity and m is the molecularly of the reaction.

$$k = \frac{k_B T}{h} K^{\ddagger} (M^{1-m}) \tag{9.19.13}$$

The following thermodynamic equations further describe the equilibrium constant:

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{9.19.14}$$
$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{9.19.15}$$

where $\Delta G^{\ddagger}$ is the Gibbs energy of activation, $\Delta H^{\ddagger}$ is the **enthalpy of activation** and $\Delta S^{\ddagger}$ is the **entropy of activation**. Combining Equations 9.19.10and 9.19.11to solve for $\ln K^{\ddagger}$ gives:

$$\ln K^{\ddagger} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} \tag{9.19.16}$$

The Eyring Equation is finally given by substituting Equation 9.19.16into Equation 9.19.12:

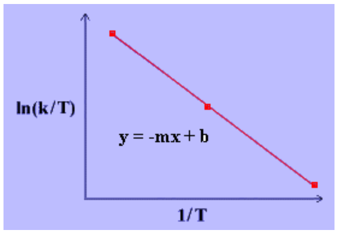
$$k = \frac{k_B T}{h} e^{-\frac{\Delta H^{\ddagger}}{RT}} e^{\frac{\Delta S^{\ddagger}}{R}} \tag{9.19.17}$$

Application of the Eyring Equation

The linear form of the Eyring Equation is given below:

$$\ln \frac{k}{T} = \frac{-\Delta H^{\dagger}}{R} \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{9.19.18}$$

The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be determined from kinetic data obtained from a $\ln \frac{k}{T}$ vs. $\frac{1}{T}$ plot. The Equation is a straight line with negative slope, $\frac{-\Delta H^{\ddagger}}{R}$, and a y-intercept, $\frac{\Delta S^{\ddagger}}{R} + \ln \frac{k_B}{h}$.



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Contributors and Attributions

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CHAPTER OVERVIEW

10: Complex Reaction Mechanisms

10.1: The Lindemann Mechanism

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. Frederick Lindemann discovered the concept in 1921 and Cyril Hinshelwood developed it. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step. The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

10.1.1: General Mechanism

The schematic reaction $A + M \rightarrow P$ is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of A

$$A + M \rightleftharpoons A^* + M \tag{10.1.1}$$

with

- forward activation reaction rate: k_1
- reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of $A*$

$$A^* \xrightarrow{k_2} P \tag{10.1.2}$$

with

- forward reaction rate: k_2

Assuming that the concentration of intermediate A^* is held constant according to the quasi steady-state approximation, what is the rate of formation of product P?

Solution

First, find the rates of production and consumption of intermediate A^*. The rate of production of A^* in the first elementary step (Equation 10.1.1) and A^* is consumed both in the reverse first step and in the forward second step. The respective rates of consumption of A^* are:

$$\frac{d[A^*]}{dt} = \underset{\text{(forward first step)}}{k_1[A][M]} - \underset{\text{(reverse first step)}}{k_{-1}[A^*][M]} - \underset{\text{(forward second step)}}{k_2[A^*]} \tag{10.1.3}$$

According to the steady-state approximation,

$$\frac{d[A^*]}{dt} \approx 0 \tag{10.1.4}$$

Therefore the rate of production of A^* (first term in Equation 10.1.3) equals the rate of consumption (second and third terms in Equation 10.1.3):

$$k_1[A][M] = k_{-1}[A^*][M] + k_2[A^*] \tag{10.1.5}$$

Solving for $[A^*]$, it is found that

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \tag{10.1.6}$$

The overall reaction rate is (Equation 10.1.2)

$$\frac{d[P]}{dt} = k_2[A^*] \tag{10.1.7}$$

Now, by substituting the calculated value for $[A^*]$ (Equation 10.1.6 into Equation 10.1.7), the overall reaction rate can be expressed in terms of the original reactants A and M as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} \tag{10.1.8}$$

The rate law for the Lindemann mechanism is not a simple first or second order reaction. However, under certain conditions (discussed below), Equation 10.1.8 can be simplified.

Three Principles of the Lindemann Mechanism

1. Energy is transferred by collision (forward reaction of Equation 10.1.1)
2. There is a time delay Δt between collision and reaction (Equation 10.1.2)
3. Molecules may be de-activated by another collision during Δt (reverse reaction of Equation 10.1.1)

Example 29.6.1 : Dissociation of

The decomposition of dinitrogen pentoxide to nitrogen dioxide and nitrogen trioxide

$$N_2O_5 \rightarrow NO_2 + NO_3$$

is postulated to take place via two elementary steps, which are similar in form to the schematic example given above:

1. $N_2O_5 + N_2O_5 \rightleftharpoons N_2O_5^* + N_2O_5$
2. $N_2O_5^* \rightarrow NO_2 + NO_3$

Using the quasi steady-state approximation soluioten (Equation 9) with $[M] = [N_2O_5]$, then rate equation is:

$$\text{Rate} = k_2[N_2O_5]^* = \frac{k_1 k_2 [N_2O_5]^2}{k_{-1}[N_2O_5] + k_2}$$

Experiment has shown that the rate is observed as first-order in the original concentration of N_2O_5 sometimes, and second order at other times.

- If $k_2 >> k_{-1}$, then the rate equation may be simplified by assuming that $k_{-1} \approx 0$. Then the rate equation is

  $$\text{Rate} = k_1[N_2O_5]^2$$

  which is *second order*.
- If $k_2 << k_{-1}$, then the rate equation may be simplified by assuming $k_2 \approx 0$. Then the rate equation is

  $$\text{Rate} = \frac{k_1 k_2 [N_2O_5]}{k_{-1}} = k_{obs}[N_2O_5]$$

  which is *first order* with

  $$k_{obs} = \frac{k_2 k_2}{k_{-1}}.$$

Exercise 29.6.1

The following first order rate constants for the gas phase decomposition of N_2O_5 have been obtained as a function of number density at 298 K.

$k_{obs}\,(s^{-1})$	7.81×10^{-3}	12.5×10^{-3}	15.6×10^{-3}
$[N_2O_5] (mol/m^{-3})$	10	25	50

> Confirm that these data are consistent with the Lindemann mechanism and derive a rate constant and a ratio of two rate constants for elementary reactions in the mechanism. What are the units of the two quantities.

10.1.2: Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN$$

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:

$$\frac{d\left[CH_3NC\right]}{dt} = -k[CH_3NC]^2 \tag{10.1.9}$$

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

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{10.1.10}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{10.1.11}$$

where M can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of 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 B with time:

$$\frac{d\left[\mathrm{A}^*\right]}{dt} = k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] - k_{-1}\left[\mathrm{A}^*\right]_{ss}\left[\mathrm{M}\right] - k_2\left[\mathrm{A}^*\right]_{ss} \approx 0 \tag{10.1.12}$$

Solving for $\left[\mathrm{A}^*\right]$,

$$\left[\mathrm{A}^*\right] = \frac{k_1\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{10.1.13}$$

The reaction rates of species A and B can be written as

$$-\frac{d\left[\mathrm{A}\right]}{dt} = \frac{d\left[\mathrm{B}\right]}{dt} = k_2\left[\mathrm{A}^*\right] = \frac{k_1k_2\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} = k_{\mathrm{obs}}\left[\mathrm{A}\right] \tag{10.1.14}$$

where

$$k_{\mathrm{obs}} = \frac{k_1k_2\left[\mathrm{M}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{10.1.15}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}\left[\mathrm{M}\right] \gg k_2$. Equation 10.1.14then becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt} = \frac{k_1k_2}{k_{-1}}\left[\mathrm{A}\right] \tag{10.1.16}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}\left[\mathrm{M}\right] \ll k_2$. In this scenario, Equation 10.1.14 becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt} = k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] \tag{10.1.17}$$

which follows second order rate kinetics, consistent with experimental observations.

10.1.3: References

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10.2: Some Reaction Mechanisms Involve Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step** – a step that consumes intermediates without creating new ones

These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{10.2.1}$$

A proposed mechanism is

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{10.2.2}$$

$$2Br^{\cdot} + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{10.2.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{10.2.4}$$

Based on this mechanism, the rate of change of concentrations for the intermediates ($H^{\cdot}$ and $Br^{\cdot}$) can be written, and the steady state approximation applied.

$$\frac{d[H^{\cdot}]}{dt} = k_2[Br^{\cdot}][H_2] - k_{-2}[HBr][H^{\cdot}] - k_3[H^{\cdot}][Br_2] = 0$$

$$\frac{d[Br^{\cdot}]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 - k_2[Br^{\cdot}][H_2] + k_{-2}[HBr][H^{\cdot}] + k_3[H^{\cdot}][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2, k_{-2}, and k_3. The result is

$$2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 = 0$$

Solving for $Br^{\cdot}$

$$Br^{\cdot} = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the $H^{\cdot}$ that is generated by solving the steady state expression for $d[H^{\cdot}]/dt$.

$$[H^{\cdot}] = \frac{k_2[Br^{\cdot}][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^{\cdot}] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $H^{\cdot}$ and $Br^{\cdot}$, we can substitute them into an expression for the rate of production of the product HBr:

$$\frac{[HBr]}{dt} = k_2[Br^{\cdot}][H_2] + k_3[H^{\cdot}][Br_2] - k_{-2}[H^{\cdot}][HBr]$$

After substitution and simplification, the result is

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}}{1+\frac{k_{-1}}{k_3}\frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2]+\frac{k_{-1}}{k_3}[HBr]}$$

which matches the form of the rate law found experimentally (Equation 10.2.1)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

10.3: Catalysis

There are many examples of reactions that involve catalysis. One that is of current importance to the chemistry of the environment is the catalytic decomposition of ozone (Fahey, 2006). The overall reaction

$$O_3 + O^{\cdot} \rightarrow 2O_2$$

can be catalyze by atomic chlorine by the following mechanism.

$$O_3 + Cl \xrightarrow{k_1} ClO + O_2$$

$$ClO + O \xrightarrow{k_1} Cl + O_2$$

The rate of change of the intermediate (ClO) concentration is given by

$$\frac{[ClO]}{dt} = k_1[O_3][Cl] - k_2[ClO][O]$$

Applying the steady state approximation to this relationship and solving for $[ClO]$ produces

$$ClO] = \frac{[O_3][Cl]}{k_2[O]} \tag{10.3.1}$$

The rate of production of O_2 (which is two times the rate of the reaction) is given by

$$\frac{d[O_2]}{dt} = k_2[O_3][Cl] + k_2[ClO][O]$$

Substituting the expression for $[ClO]$ (Equation 10.3.1) into the above expression yields

$$\begin{aligned} \frac{d[O_2]}{dt} &= k_2[O_3][Cl] + k_2\left(\frac{[O_3][Cl]}{k_2[O]}\right)[O] \\ &= k_1[O_3[Cl] + k_1[O_3][Cl] \\ &= 2k_1[O_3][Cl] \end{aligned}$$

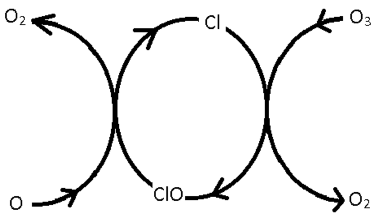
And so the rate of the reaction is predicted to be first order in $[O_3]$, first order in the catalyst $[Cl]$, and second order overall.

$$\text{rate} = k[O_3][Cl]$$

If the concentration of the catalyst is constant, the reaction kinetics will reduce to first order.

$$\text{rate} = k[O_3]$$

This catalytic cycle can be represented in the following diagram:



On the left, atomic oxygen picks up an oxygen atom from ClO to form O_2 and generate a Cl atom, which can then react with O_3 to form ClO and an O_2 molecule. The closed loop in the middle is characteristic of the catalytic cycle involving Cl and ClO. Further, since Cl acts as a catalyst, it can decompose many O_3 molecules without being degraded through side reactions.

The introduction of chlorine atoms into the upper atmosphere is a major environmental problem, leading to the annual thinning and eventual opening of the ozone layer over Antarctica. The source of chlorine is from the decomposition of chlorofluorocarbons which are sued as refrigerants and propellants due to their incredible stability near the Earth's surface. However, in the upper atmosphere, these compounds are subjected to ultraviolet radiation emitted by the sun and decompose to form the radicals responsible for the catalytic decomposition of ozone. The world community addressed this issue by drafting the **Montreal Protocol (Secretariat, 2015)**, which focused on the emission of ozone-destroying compounds. The result of this action has brought about evidence of the Antarctic ozone hole healing (K, 2015). This is one very good example science-guided political, industrial, and economic policies leading to positive changes for our environment.

10.4: The Michaelis-Menten Mechanism

The **Michaelis-Menten** mechanism (Michaelis & Menten, 1913) is one which many enzyme mitigated reactions follow. The basic mechanism involves an enzyme (E, a biological catalyst) and a substrate (S) which must connect to form an enzyme-substrate complex (ES) in order for the substrate to be degraded (or augmented) to form a product (P). The overall reaction is

$$S \rightarrow P$$

And the simple two-step mechanism is given by

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \tag{10.4.1}$$

$$ES \xrightarrow{k_2} P \tag{10.4.2}$$

Notice that the enzyme is necessary for the reaction to proceed, but is not part of the overall stoichiometry (as is the case for any catalyst!).

Equilibrium Approximation Derivation

Applying the equilibrium approximation to the first step

$$k_1[E][S] \approx k_{-1}[ES] \tag{10.4.3}$$

And using a mass conservation relationship on the enzyme (noting that the enzyme must be either in its bare form (E) or complexed with a substrate (ES)):

$$[E]_o = [E] + [ES]$$

or

$$[E] = [E]_o - [ES]$$

Substituting this into the equilibrium expression (Equation 10.4.3) yields

$$k_1([E]_o - [ES])[S] = k_{-1}[ES]$$

Solving this expression for $[ES]$ stepwise reveals

$$k_1[E]_o[S] - k_1[ES][S] = k_{-1}[ES]$$

$$k_1[E]_o[S] = k_{-1}[ES] + k_1[ES][S]$$

$$= (k_{-1} + k_1)[ES]$$

$$\frac{k_1[E]_o[S]}{k_1[S] + k_{-1}} = [ES]$$

Substituting this into the expression for the rate of production of the product P

$$\frac{d[P]}{dt} = k_2[ES] \tag{10.4.4}$$

yields

$$\frac{d[P]}{dt} = \frac{k_2 k_1[E]_o[S]}{k_1[S] + k_{-1}}$$

Multiplying the top and bottom of the expression on the right hand side by 1/k$_1$ gives the result

$$\frac{d[P]}{dt} = \frac{k_2[E]_o[S]}{[S] + \frac{k_1}{k_{-1}}}$$

The ratio of k_{-1}/k_1 is the equilibrium constant that describes the dissociation of the enzyme-substrate complex, K_d in Equation 10.4.1. Noting that $k_2[E]_0$ gives the maximum rate (V_{max}), and that $\frac{d[P]}{dt}$ is the observed reaction rate, the rate law takes the form

$$\text{rate} = \frac{V_{max}[S]}{K_d + [S]}$$

> This is because the maximum reaction rate is achieved when [ES] is low. As [ES] increases, the likelihood of the complex decomposing to reform reactants is higher, slowing the conversion. [ES] will be low if the concentration of the enzyme is much larger than that of the substrate, so there is never a shortage of enzyme available to form the complex with the substrate. However, if the substrate concentration is higher, the lack of available enzyme active sites will slow the reaction and cause it to become 0th order.

In the limit that the substrate concentration is large compared to K_d (i.e., $K_d + [S] \approx [S]$), the reaction ends up zeroth order in substrate.

$$\text{rate} = \frac{V_{max}[S]}{K_d + [S]} \approx \frac{V_{max}\ \cancel{[S]}}{\cancel{[S]}} = V_{max}$$

Hence, adding more substrate to the system under this limiting condition will have no effect on the observed rate. This is characteristic of a bottleneck in the mechanism, which would happen if there is a shortage of enzyme sites to which the substrate can attach.

In the other extreme, in which K_d is very large compared to the substrate concentration (i.e., $K_d + [S] \approx K_d$), the reaction become first order in substrate.

$$\text{rate} = \frac{V_{max}[S]}{K_d + [S]} \approx \frac{V_{max}[S]}{K_d} = \frac{V_{max}}{K_d}[S]$$

Steady-State Approximation Derivation

In an alternate derivation (Briggs & Haldane, 1925) using the steady state approximation applied to the enzyme-substrate complex

$$\frac{[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] \approx 0$$

Solving for $[ES]$ gives the result

$$ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$$

or

$$[ES] = \frac{[E][S]}{K_m}$$

where

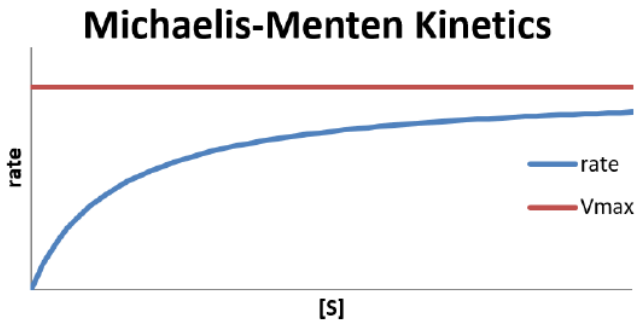
$$K_m = \frac{k_{-1} + K_2}{k_1}$$

K_M is the **Michaelis constant**, which is affected by a number of factors, including pH, temperature, and the nature of the substrate itself. Proceeding as before, though the conservation of mass relationship and substitution into the expression for rate (Equation 10.4.4) results in

$$\frac{d[P]}{dt} = \frac{V_{max}[S]}{K_m + [S]}$$

The advantage to this approach is that it accounts for the loss of ES complex due to the production of products as well as the decomposition to reform the reactants E and S. As before, in the limit that $[S] \gg K_M$, the reaction reaches its maximum rate (

V_{max}) and becomes independent of any concentrations. However in the limit that $[S] \ll K_M$, the reaction becomes 1st order in $[S]$.



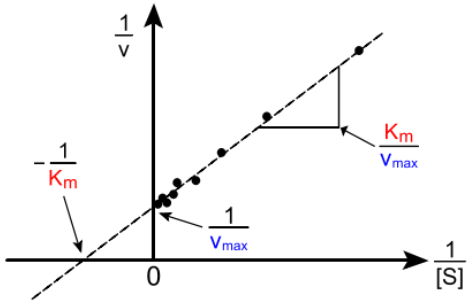
The Michalis constant and V_{max} parameters can be extracted in a number of ways. In the Lineweaver-Burk (Lineweaver & Burk, 1934) method, the reciprocal of the rate law is used to create a linear relationship.

$$\frac{1}{\text{rate}} = \frac{K_m + [S]}{V_{max}[S]}$$

or

$$\frac{1}{\text{rate}} = \frac{K_m}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}}$$

So a plot of $1/rate$ as a function of $1/[S]$ results in a straight line, the slope of which is equal to K_M/V_{max} and the intercept is $1/V_{max}$. This is called a Lineweaver–Burk plot.



An example of a Lineweaver-Burk plot. (CC BY-SA 3.0; Diberri).

10.5: Isotherms are Plots of Surface Coverage as a Function of Gas Pressure at Constant Temperature

10.5.1: Introduction

Whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid. As with all chemical equilibria, the position of equilibrium will depend upon a number of factors:

1. The relative stabilities of the adsorbed and gas phase species involved
2. The temperature of the system (both the gas and surface, although these are normally the same)
3. The pressure of the gas above the surface

In general, factors (2) and (3) exert opposite effects on the concentration of adsorbed species - that is to say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

The Langmuir isotherm was developed by Irving Langmuir in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. There are many other types of isotherm (Temkin, Freundlich ...) which differ in one or more of the assumptions made in deriving the expression for the surface coverage; in particular, on how they treat the surface coverage dependence of the enthalpy of adsorption. Whilst the Langmuir isotherm is one of the simplest, it still provides a useful insight into the pressure dependence of the extent of surface adsorption.

Note: Surface Coverage & the Langmuir Isotherm

When considering adsorption isotherms it is conventional to adopt a definition of **surface coverage** (θ) which defines the maximum (saturation) surface coverage of a particular adsorbate on a given surface always to be unity, i.e. $\theta_{max} = 1$. This way of defining the surface coverage differs from that usually adopted in surface science where the more common practice is to equate θ with the ratio of adsorbate species to surface substrate atoms (which leads to saturation coverages which are almost invariably less than unity).

10.5.2: The Langmuir Isotherm - Derivation from Equilibrium Considerations

We may derive the Langmuir isotherm by treating the adsorption process as we would any other equilibrium process - except in this case the equilibrium is between the gas phase molecules (M), together with vacant surface sites, and the species adsorbed on the surface. Thus, for a non-dissociative (molecular) adsorption process, we consider the adsorption to be represented by the following chemical equation :

$$S-* + M_{(g)} \rightleftharpoons S-M \tag{10.5.1}$$

where :

- $S-*$ represents a vacant surface site

10.5.2.1: Assumption 1

In writing Equation ref{Eq1} we are making an inherent assumption that there are a fixed number of localized surface sites present on the surface. This is the first major assumption of the Langmuir isotherm.

We may now define an equilibrium constant (K) in terms of the concentrations of "reactants" and "products"

$$K = \frac{[S-M]}{[S-*][M]} \tag{10.5.2}$$

We may also note that :The [S - M] is proportional to the surface coverage of adsorbed molecules, i.e. proportional to θ

- [S - *] is proportional to the number of vacant sites, i.e. proportional to $1-\theta$
- [M] is proportional to the pressure of gas, \(P\)

Hence, it is also possible to define another equilibrium constant, b , as given below :

$$b = \frac{\theta}{(1-\theta)P} \tag{10.5.3}$$

Rearrangement then gives the following expression for the surface coverage

$$\theta = \frac{bP}{1+bP} \tag{10.5.4}$$

which is the usual form of expressing the Langmuir Isotherm. As with all chemical reactions, the equilibrium constant, b, is both temperature-dependent and related to the Gibbs free energy and hence to the enthalpy change for the process.

10.5.2.2: Assumption 2

b is only a constant (independent of θ) if the enthalpy of adsorption is independent of coverage. This is the second major assumption of the Langmuir Isotherm.

A plot of θ vs. bP shows that as the pressure increases, θ approaches 1, meaning that nearly the entire surface is coated with a monolayer of adsorbed gas (Figure $10.5.1$).

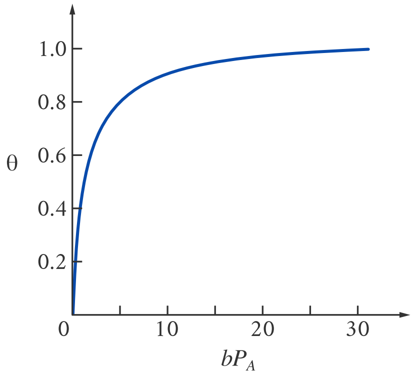


Figure 10.5.1: A plot of equation 10.5.4 which shows the nonlinear relationship between the fraction of surface coverage and the gas pressure. .(CC BY-NC; Ümit Kaya via LibreTexts)

Equation $10.5.4$can be rearranged to the form

$$\frac{1}{\theta} = 1 + \frac{1}{bP} \tag{10.5.5}$$

showing that the inverse of the fraction of occupied surface sites is a linear function of the inverse of the pressure. If we plot experimental data for the adsorption of diatomic oxygen and carbon monoxide onto a silica surface, we can see that the Langmuir adsorption isotherm describes the data well (figure $10.5.2$).

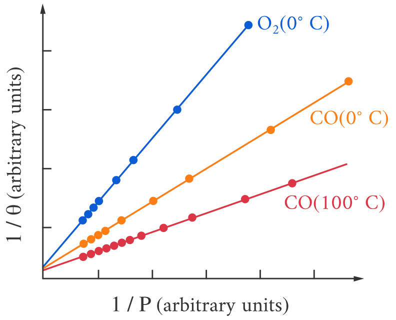


Figure 10.5.2: A plot showing the relationship of the inverse of the fraction of occupied surface sites to the inverse of the gas pressure for O_2 and CO molecules adsorbed onto a silica surface. (CC BY-NC; Ümit Kaya via LibreTexts)

10.5.3: The Langmuir Isotherm from a Kinetics Consideration

The equilibrium that may exist between gas adsorbed on a surface and molecules in the gas phase is a dynamic state, i.e. **the equilibrium represents a state in which the rate of adsorption of molecules onto the surface is exactly counterbalanced by**

the rate of desorption of molecules back into the gas phase. It should therefore be possible to derive an isotherm for the adsorption process simply by considering and equating the rates for these two processes.

Expressions for the rate of adsorption and rate of desorption have been derived in Sections 2.3 & 2.6 respectively: specifically ,

$$R_{ads} = \frac{f(\theta)P}{\sqrt{2\pi mkT}} \exp(-E_a^{ads}/RT)$$

$$R_{des} = v\ f'(\theta) \exp(-E_a^{ads}/RT)$$

Equating these two rates yields an equation of the form :

$$\frac{P\ f(\theta)}{f'(\theta)} = C(T) \tag{10.5.6}$$

where θ is the fraction of sites occupied at equilibrium and the terms $f(\theta)$ and $f'(\theta)$ contain the pre-exponential surface coverage dependence of the rates of adsorption and desorption respectively and all other factors have been taken over to the right hand side to give a temperature-dependent "constant" characteristic of this particular adsorption process, $C(T)$. We now need to make certain simplifying assumptions. The first is one of the key assumptions of the Langmuir isotherm.

Assumption 1

Adsorption takes place only at specific localized sites on the surface and the saturation coverage corresponds to complete occupancy of these sites.

Let us initially further restrict our consideration to a simple case of **reversible molecular adsorption**, i.e.

$$S - * + \mathrm{M_{(g)}} \rightleftharpoons \mathrm{S{-}M} \tag{10.5.7}$$

where

- $S - *$ represents a vacant surface site and
- S−M the adsorption complex.

Under these circumstances it is reasonable to assume coverage dependencies for rates of the two processes of the form :

- **Adsorption** (forward reaction in Equation 10.5.7):

  $$f(\theta) = c(1-\theta) \tag{10.5.8}$$

  i.e. proportional to the fraction of sites that are unoccupied.
- **Desorption** (reverse reaction in Equation 10.5.7):

  $$f'(\theta) = c'\theta \tag{10.5.9}$$

  i.e. proportional to the fraction of sites which are occupied by adsorbed molecules.

Note

These coverage dependencies in Equations 10.5.8 and 10.5.9 are exactly what would be predicted by noting that the forward and reverse processes are elementary reaction steps, in which case it follows from standard chemical kinetic theory that

- The forward adsorption process will exhibit kinetics having a first order dependence on the concentration of vacant surface sites and first order dependence on the concentration of gas particles (proportional to pressure).
- The reverse desorption process will exhibit kinetics having a first order dependence on the concentration of adsorbed molecules.

Substitution of Equations 10.5.8 and 10.5.9 into Equation 10.5.6 yields:

$$\frac{P(1-\theta)}{\theta} = B(T)$$

where

$$B(T) = \left(\frac{c'}{c}\right) C(T).$$

After rearrangement this gives the *Langmuir Isotherm* expression for the surface coverage

$$\theta = \frac{bP}{1 + bP}$$

where $b = 1/B(T)$ is a function of temperature and contains an exponential term of the form

$$b \propto \exp[(E_a^{des} - E_a^{ads})/RT] = \exp[-\Delta H_{ads}/RT]$$

with

$$\Delta H_{ads} = E_a^{des} - E_a^{ads}.$$

Assumption 2

b can be regarded as a **constant** with respect to coverage only if the enthalpy of adsorption is itself **independent** of coverage; this is the second major assumption of the Langmuir Isotherm.

10.5.4: Contributors and Attributions

- Roger Nix (Queen Mary, University of London)

10.6: Atoms and Molecules can Physisorb or Chemisorb to a Surface

In this section, we will consider both the energetics of adsorption and factors which influence the kinetics of adsorption by looking at the "potential energy diagram/curve" for the adsorption process. The potential energy curve for the adsorption process is a representation of the variation of the energy (PE or E) of the system as a function of the distance (d) of an adsorbate from a surface.

Within this simple one-dimensional (1D) model, the only variable is the distance (d) of the adsorbing molecule from the substrate surface (Figure $10.6.1$).

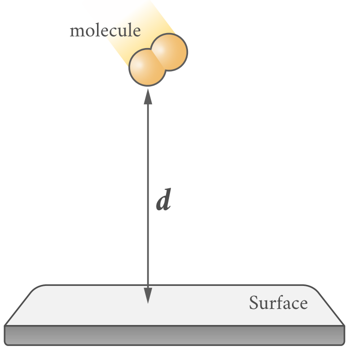


Figure 10.6.1: A particle approaching a solid surface. (CC BY-NC; Ümit Kaya via LibreTexts)

Thus, the energy of the system is a function only of this variable i.e.

$$E = E(d)$$

It should be remembered that this is a very simplistic model which neglects many other parameters which influence the energy of the system (a single molecule approaching a clean surface), including for example

- *the angular orientation of the molecule*
- *changes in the internal bond angles and bond lengths of the molecule*
- *the position of the molecule parallel to the surface plane*

The interaction of a molecule with a given surface will also clearly be dependent upon the presence of any existing adsorbed species, whether these be surface impurities or simply pre-adsorbed molecules of the same type (in the latter case we are starting to consider the effect of surface coverage on the adsorption characteristics). Nevertheless, it is useful to first consider the interaction of an isolated molecule with a clean surface using the simple 1D model. For the purposes of this section, we will also not be overly concerned whether the "energy" being referred to should strictly be the internal energy, the enthalpy or free energy of the system. We will also make a distinction between physisorption and chemisorption. These two types of interaction with a surface are differentiated by the strength of interaction bewteen the adsorbed particle and the surface. A physisorbed particle will always be farther away from the surface than an identical particle that is chemisorbed (Figures $10.6.2$ and $10.6.3$).

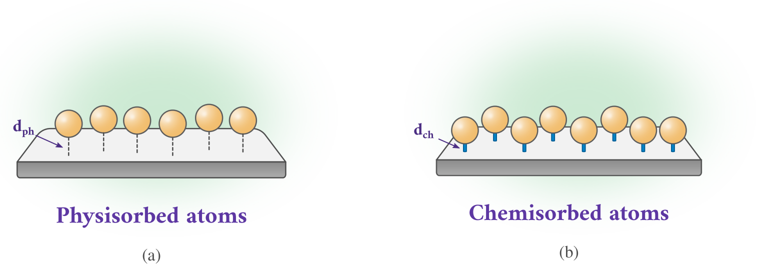
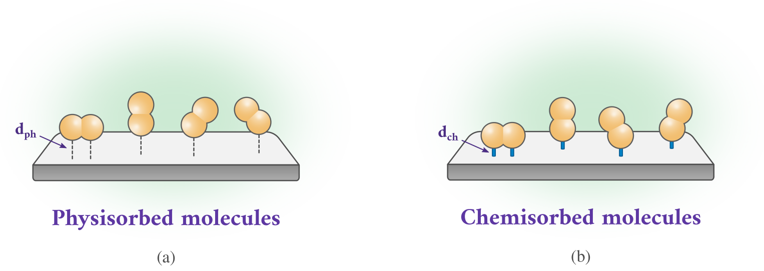


Figure 10.6.2: a) A picture of physisorbed atoms. The atoms are, on average, a distance of d_{ph} from the surface. b) A picture of chemisorbed atoms. The atoms are, on average, a distance of d_{ch} from the surface. Note that d_{ph} is always greater than d_{ch}. (CC BY-NC; Ümit Kaya via LibreTexts)



(a) (b)

Figure 10.6.3: a) A picture of physisorbed molecules. The molecules are, on average, a distance of d_{ph} from the surface. Note that the molecules can adsorb to the surface at various orientations. b) A picture of chemisorbed molecules. The molecules are, on average, a distance of d_{ch} from the surface. Note that the molecules can adsorb to the surface at various orientations. Also note that d_{ph} is always greater than d_{ch}. (CC BY-NC; Ümit Kaya via LibreTexts)

10.6.1: CASE I - Physisorption

In the case of pure physisorption, e.g., Ar/metals, the only attraction between the adsorbing species and the surface arises from weak, van der Waals forces. As illustrated in Figure 10.6.4 below, these forces give rise to a shallow minimum in the PE curve at a relatively large distance from the surface (typically $d > 0.3\,nm$) before the strong repulsive forces arising from electron density overlap cause a rapid increase in the total energy.

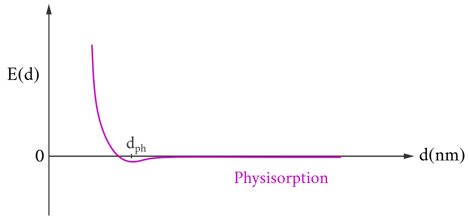


Figure 10.6.4: A graph showing the potential energy change as a particle moves closer and closer to a surface and eventually physisorbs onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

There is no barrier to prevent the atom or molecule which is approaching the surface from entering this physisorption well, i.e. the process is not activated and the kinetics of physisorption are invariably fast.

10.6.2: CASE II - Physisorption + Molecular Chemisorption

The weak physical adsorption forces and the associated long-range attraction will be present to varying degrees in all adsorbate/substrate systems. However, in cases where chemical bond formation between the adsorbate and substrate can also occur, the PE curve is dominated by a much deeper chemisorption minimum at shorter values of d, as shown in Figure 10.6.5.

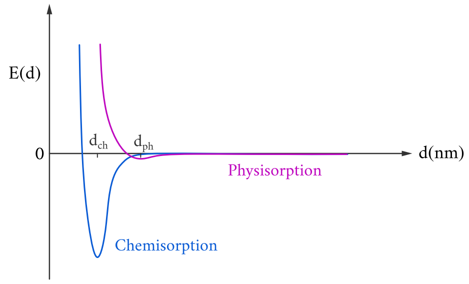


Figure 10.6.5: A graph showing the potential energy change as a particle moves closer and closer to a surface to eventually either physisorb or chemisorb onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

The graph above shows the PE curves due to physisorption and chemisorption separately. In practice, the PE curve for any real molecule capable of undergoing chemisorption is best described by a combination of the two curves, with a curve crossing at the point at which chemisorption forces begin to dominate over those arising from physisorption alone (Figure 10.6.6).

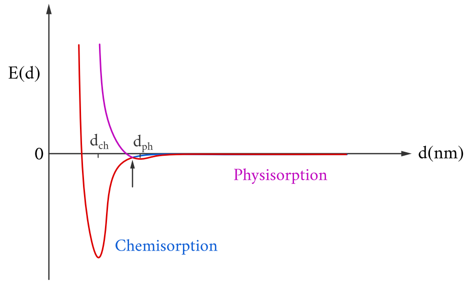


Figure 10.6.6: The red curve is a graph showing the potential energy change as a particle moves closer and closer to a surface, eventually physisorping onto the surface, and then undergoing chemisorption onto that same surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. The vertical arrow points to the crossover point at which the particle approaches close enough to the surface for the forces of chemisorption to dominate. (CC BY-NC; Ümit Kaya via LibreTexts)

The minimum energy pathway obtained by combining the two PE curves is now highlighted in red. Any perturbation of the combined PE curve from the original, separate curves is most likely to be evident close to the highlighted crossing point.

For clarity, we will now consider only the overall PE curve as shown in Figure 10.6.7:

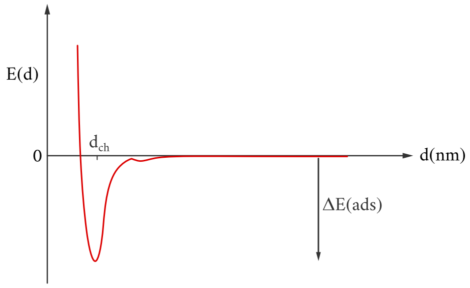


Figure 10.6.7: A graph showing the potential energy change as a particle moves closer and closer to a surface, eventually physisorbing onto the surface, and then undergoing chemisorption onto that same surface. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. The energy of adsorption is represented by $\Delta E(ads)$. (CC BY-NC; Ümit Kaya via LibreTexts)

The depth of the chemisorption well is a measure of the strength of binding to the surface. In fact, it is a direct representation of the energy of adsorption, whilst the location of the global minimum on the horizontal axis corresponds to the equilibrium bond distance (d_{ch}) for the adsorbed molecule on this surface.

The energy of adsorption is *negative*, and because it corresponds to the energy *change* upon adsorption, it is better represented as ΔE (ads) or ΔE_{ads} . However, you will also often find the depth of this well associated with the enthalpy of adsorption, ΔH (ads).

> *The "heat of adsorption", Q, is taken to be a positive quantity equal in magnitude to the enthalpy of adsorption ; i.e. Q = -ΔH(ads))*

In this particular case, there is clearly no barrier to be overcome in the adsorption process and there is no activation energy of adsorption (i.e. $E_a^{ads} = 0$, but do remember the previously mentioned limitations of this simple 1D model). There is of course a significant barrier to the reverse, desorption process; the red arrow in Figure 10.6.8 below represents the activation energy for desorption.

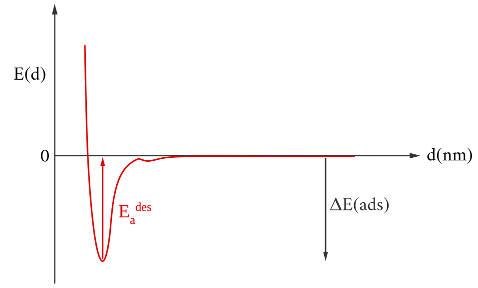


Figure 10.6.8: A graph showing both the energy of adsorption, $\Delta E(ads)$, and the activation energy of desorption, E_a^{des}. (CC BY-NC; Ümit Kaya via LibreTexts)

Clearly, in this particular case, the magnitudes of the energy of adsorption and the activation energy for desorption can also be equated i.e.

$$E_a^{des} = \Delta E(ads)$$

or

$$E_a^{des} \approx -\Delta H(ads)$$

10.6.3: CASE III - Physisorption + Dissociative Chemisorption

In this case, the main differences arise from the substantial changes in the PE curve for the chemisorption process. Again, we start off with the basic PE curve (Figure $10.6.9$) for the physisorption process which represents how the molecule can weakly interact with the surface :

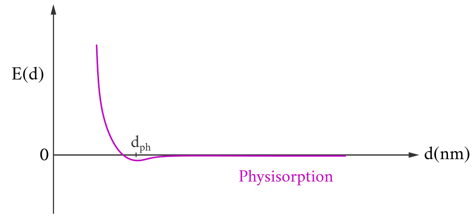


Figure 10.6.9: A graph showing the potential energy change as a particle moves closer and closer to a surface and eventually physisorbs onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

If we now consider a specific molecule such as H_2 and initially treat it as being completely **isolated** from the surface (i.e. when the distance, *d*, is very large), then a substantial amount of energy would need to be put into the system in order to cause dissociation of the molecule.

$$\mathrm{H_2 \rightarrow H + H}$$

This amount of required energy is the bond dissociation energy $D_{(H-H)}$, which is some 435 kJ mol^{-1} or 4.5 eV.

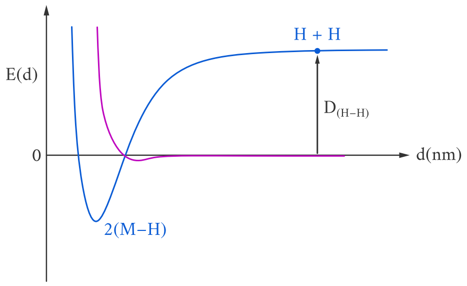


Figure 10.6.10: A graph showing the potential energy changes involved in the dissociation of an H2 molecule. An H2 molecule very far away from the surface has two paths by which it can end up as two separate H atoms chemisorbed onto the surface. (a) An input of 435 kJ per mole will break of the H-H bond. The separate H atoms can then eventually approach the surface and bond to it. (The red pathway) (b) The H2 molecule can approach the surface, physisorb onto the surface, and then undergo dissociative chemisorption. (Starting on the right on the purple pathway, then switching to the red pathway at the crossover point.) (CC BY-NC; Ümit Kaya via LibreTexts)

The red dot in Figure 10.6.10 above thus represents two hydrogen atoms, equidistant (and a long distance) from the surface, and also now well separated from each other. If these atoms are then allowed to approach the surface they may ultimately both form strong chemical bonds to the substrate. This possible bonding of two H atoms to the surface (shown as 2(M-H) in the Figure) corresponds to the minimum in the red curve which represents the chemisorption PE curve for the two H atoms.

In reality, of course, such a mechanism for dissociative hydrogen chemisorption is not practical; the energy down payment associated with breaking the H-H bond is far too severe. Instead, a hydrogen molecule will initially approach the surface along the physisorption curve. If it has sufficient energy it may pass straight into the chemisorption well ("direct chemisorption") as shown below in Figure 10.6.11.

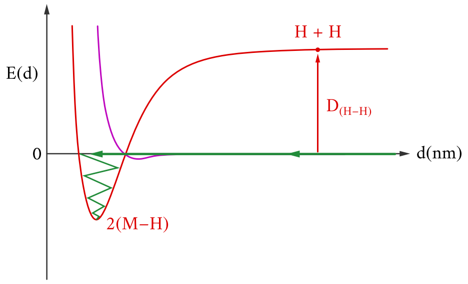


Figure 10.6.11: A graph showing the potential energy changes involved in the direct chemisorption of an H2 molecule. The H2 molecule approaches the surface following the green pathway, bypasses physisorption, and instead undergoes direct dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

Alternatively, the hydrogen molecule may first undergo transient physisorption, a state from which it can then either desorb back as a molecule into the gas phase or cross over the barrier into the dissociated, chemisorptive state (as illustrated *schematically* in Figure 10.6.12).

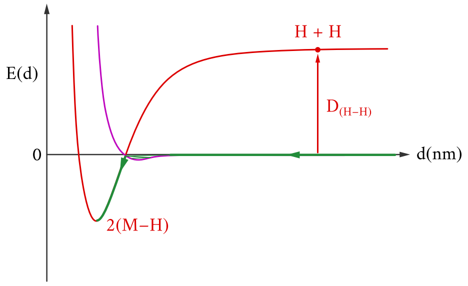


Figure 10.6.12: A graph showing the potential energy changes involved in the precursor-mediated chemisorption of an H_2 molecule. The H_2 molecule approaches the surface following the green pathway, first undergoes physisorption, and then undergoes dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

In this latter case, the molecule can be said to have undergone "precursor-mediated" chemisorption. A picture of the process of the approach, physisorption, and dissociative chemisorption of a molecule is shown in Figure 10.6.13. The molecule in this picture is following the general potential energy pathway described in either Figure 10.6.11or Figure 10.6.12

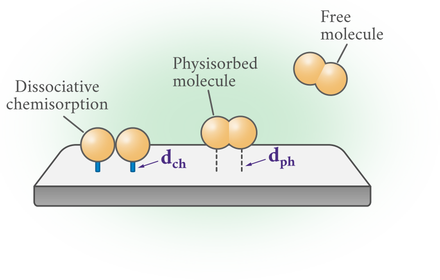


Figure 10.6.13: The sequential process of a free molecule approaching a surface, becoming physisrobed onto the surface, and eventually undergoing dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

The characteristics of this type of dissociative adsorption process are clearly going to be strongly influenced by the position of the crossing point of the two curves (molecular physisorption versus dissociative chemisorption) - relatively small shifts in the position of either of the two curves can significantly alter the size of any barrier to chemisorption.

In the example shown in Figure 10.6.14below there is no direct activation barrier to dissociative adsorption - the curve crossing is below the initial "zero energy" of the system.

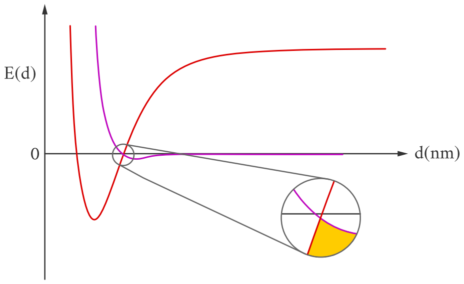


Figure 10.6.14: The potential energy pathway for physisorption followed by dissociative adsorption in which there is no direct activation barrier. (CC BY-NC; Ümit Kaya via LibreTexts)

In the case shown in Figure 10.6.15, there is a substantial barrier to chemisorption. Such a barrier has a major influence on the **kinetics** of adsorption.

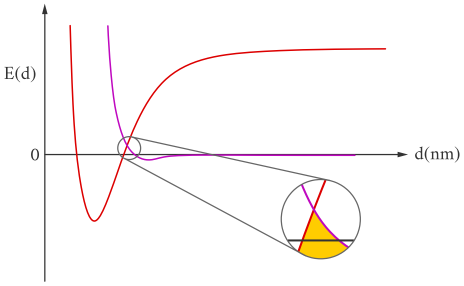


Figure 10.6.15: The potential energy pathway for physisorption followed by dissociative adsorption in which there is an activation barrier. ((CC BY-NC; Ümit Kaya via LibreTexts)

> *The depth of the physisorption well for the hydrogen molecule is actually very small (in some cases negligible), but this is not the case for other molecules and does not alter the basic conclusions regarding dissociative adsorption that result from this model; namely that the process may be either activated or non-activated depending on the exact location of the curve crossing.*

At this point, it is useful to return to consider the effect of such a barrier on the relationship between the activation energies for adsorption and desorption, and the energy (or enthalpy) of adsorption.

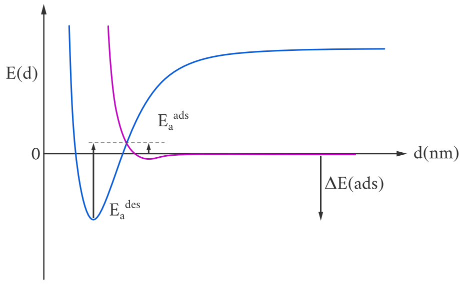


Figure 10.6.16: A comparison of the activation energy of adsorption E_a^{ads}, the activation energy of desorption E_a^{des}, and the energy of adsorption for a molecule that undergoes physisorption, directly followed by dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 10.6.16,

$$E_a^{des} - E_a^{ads} = -\Delta E_{ads}$$

but, because the activation energy for adsorption is nearly always very much smaller than that for desorption, and the difference between the energy and the enthalpy of adsorption is also very small, it is still quite common to see the relationship

$$E_a^{des} \approx -\Delta H_{ads}$$

For a slightly more detailed treatment of the adsorption process, you are referred to the following examples of More Complex PE Curves & Multi-Dimensional PE Surfaces.

10.6.4: Contributors and Attributions

Roger Nix (Queen Mary, University of London)

10.7: Using Langmuir Isotherms to Derive Rate Laws for Surface-Catalyzed Gas-Phase Reactions

It is possible to predict how the kinetics of certain heterogeneously-catalyzed reactions might vary with the partial pressures of the reactant gases above the catalyst surface by using the Langmuir isotherm expression for equilibrium surface coverages.

10.7.1: Unimolecular Decomposition

Consider the surface decomposition of a molecule A, i.e. the process

$$A_{(g)} \rightleftharpoons A_{(ads)} \rightarrow \text{Products}$$

Let us assume that :

1. The decomposition reaction occurs uniformly across the surface sites at which molecule A may be adsorbed and is not restricted to a limited number of special sites.
2. The products are very weakly bound to the surface and, once formed, are rapidly desorbed.
3. The rate determining step (rds) is the surface decomposition step.

Under these circumstances, the molecules of A adsorbed on the surface are in equilibrium with those in the gas phase and we may predict the surface concentration of A from the Langmuir isotherm, i.e.

$$\theta = \frac{bP}{1+bP}$$

The rate of the surface decomposition (and hence of the reaction) is given by an expression of the form

$$\text{rate} = k\theta$$

This is assuming that the decomposition of $A(ads)$ occurs in a simple unimolecular elementary reaction step and that the kinetics are first order with respect to the surface concentration of this adsorbed intermediate). Substituting for the coverage, θ, gives us the required expression for the rate in terms of the pressure of gas above the surface

$$\text{rate} = \frac{kbP}{1+bP} \tag{10.7.1}$$

It is useful to consider two extremes:

10.7.1.1: Low Pressure/Binding Limit

This is the low pressure (or weak binding. i.e., small b) limit : under these conditions the steady state surface coverage, θ, of the reactant molecule is very small.

$$bP \ll 1$$

then

$$1+bP \approx 1$$

and Equation 10.7.1can be simplified to

$$\text{rate} \approx kbP$$

Under this limiting case, the kinetics follow a first order reaction (with respect to the partial pressure of A) with an apparent first order rate constant $k' = kb$.

10.7.1.2: High Pressure/Binding Limit

This is the high pressure (or strong binding, i.e., large b) limit: under these conditions the steady state surface coverage, θ, of the reactant molecule is almost unity and

$$bP \gg 1$$

then

$$1+bP \approx bP$$

and Equation 10.7.1can be simplified to

$$rate \approx k$$

Under this limiting case, the kinetics follow a zero-order reaction (with respect to the partial pressure of A). The rate shows the same pressure variation as does the surface coverage, but this is hardly surprising since it is directly proportional to θ.

These two limiting cases can be identified in the general kinetics from Equation 10.7.1in Figure 10.7.1.

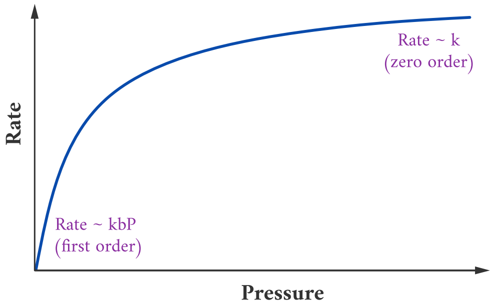


Figure 10.7.1: Plot of reaction rate versus the pressure of the reactant gas. The graph shows that at low pressures, the rate is first order with respect to the pressure of the reacting gas. At high pressures, however, the reaction approaches zero order with respect to the reacting gas.

10.7.2: Bimolecular Reaction (between molecular adsorbates)

Consider a Langmuir-Hinshelwood reaction of the following type:

$$A_{(g)} \rightleftharpoons A_{(ads)} \tag{10.7.2}$$

$$B_{(g)} \rightleftharpoons B_{(ads)} \tag{10.7.3}$$

$$A_{(ads)} + B_{(ads)} \xrightarrow{slow} AB_{(ads)} \xrightarrow{fast} AB_{(g)} \tag{10.7.4}$$

We will further assume, as noted in the above scheme, that the surface reaction between the two adsorbed species (left side of Equation 10.7.4is the rate determining step.

If the two adsorbed molecules are mobile on the surface and freely intermix then the rate of the reaction will be given by the following rate expression for the **bimolecular** surface combination step

$$Rate = k\theta_A\theta_B$$

For a single molecular adsorbate the surface coverage (as given by the standard Langmuir isotherm) is

$$\theta = \frac{bP}{1+bP}$$

Where two molecules (A & B) are competing for the same adsorption sites then the relevant expressions are (see derivation):

$$\theta_A = \frac{b_AP_A}{1+b_AP_A+b_BP_B}$$

and

$$\theta_B = \frac{b_BP_B}{1+b_AP_A+b_BP_B}$$

Substituting these into the rate expression gives :

$$Rate = k\theta_A\theta_B = \frac{kb_AP_Ab_BP_B}{(1+b_AP_A+b_BP_B)^2}$$

Once again, it is interesting to look at several extreme limits

10.7.2.1: Low Pressure/Binding Limit

$$b_A P_A \ll 1$$

and

$$b_B P_B \ll 1$$

In this limit that θ_A & θ_B are both very low , and

$$rate \rightarrow k b_A P_A b_B P_B = k' P_A P_B$$

i.e. *first order* in both reactants

10.7.2.2: Mixed Pressure/Binding Limit

$$b_A P_A \ll 1 \ll b_B P_B$$

In this limit $\theta_A \rightarrow 0$, $\theta_B \rightarrow 1$, and

$$Rate \rightarrow \frac{k b_A P_A}{b_B P_B} = \frac{k' P_A}{P_B}$$

i.e. *first order* in A, but *negative first order* in B

Clearly, depending upon the partial pressure and binding strength of the reactants, a given model for the reaction scheme can give rise to a variety of apparent kinetics: this highlights the dangers inherent in the reverse process - namely trying to use kinetic data to obtain information about the reaction mechanism.

✓ Example 10.7.1: CO Oxidation Reaction

On precious metal surfaces (e.g. Pt), the CO oxidation reaction is generally believed to by a *Langmuir-Hinshelwood mechanism* of the following type :

$$CO_{(g)} \rightleftharpoons CO_{(ads)}$$

$$O_{2(g)} \rightleftharpoons 2O_{(ads)}$$

$$CO_{(ads)} + O_{(ads)} \xrightarrow{slow} CO_{2(ads)} \xrightarrow{fast} CO_{2(g)}$$

As CO_2 is comparatively weakly-bound to the surface, the desorption of this product molecule is relatively fast and in many circumstances it is the surface reaction between the two adsorbed species that is the rate determining step.

If the two adsorbed molecules are assumed to be mobile on the surface and freely intermix then the rate of the reaction will be given by the following rate expression for the bimolecular surface combination step

$$Rate = k\,\theta_{CO}\,\theta_O$$

Where two such species (one of which is molecularly adsorbed, and the other dissociatively adsorbed) are competing for the same adsorption sites then the relevant expressions are (see derivation):

$$\theta_{CO} = \frac{b_{CO} P_{CO}}{1 + \sqrt{b_O P_{O_2}} + b_{CO} P_{CO}}$$

and

$$\theta_O = \frac{\sqrt{b_O P_{O_2}}}{1 + \sqrt{b_O P_{O_2}} + b_{CO} P_{CO}}$$

Substituting these into the rate expression gives:

$$rate = k\theta_{CO}\theta_O = \frac{kb_{CO}P_{CO}\sqrt{b_OP_{O_2}}}{(1+\sqrt{b_OP_{O_2}}+b_{CO}P_{CO})^2} \tag{10.7.5}$$

Once again, it is interesting to look at certain limits. If the CO is much more strongly bound to the surface such that

$$b_{CO}P_{CO} \gg 1+\sqrt{b_OP_{O_2}}$$

then

$$1+\sqrt{b_OP_{O_2}}+b_{CO}P_{CO} \approx b_{CO}P_{CO}$$

and the Equation 10.7.5 simplifies to give

$$rate \approx \frac{k\sqrt{b_OP_{O_2}}}{b_{CO}P_{CO}} = k'\frac{P_{O_2}^{1/2}}{P_{CO}}$$

In this limit the kinetics are half-order with respect to the gas phase pressure of molecular oxygen, but negative order with respect to the CO partial pressure, i.e. CO acts as a poison (despite being a reactant) and increasing its pressure slows down the reaction. This is because the CO is so strongly bound to the surface that it blocks oxygen adsorbing, and without sufficient oxygen atoms on the surface the rate of reaction is reduced.

10.7.3: Contributors and Attributions

- Roger Nix (Queen Mary, University of London)

10.8: The Structure of a Surface is Different from that of a Bulk Solid

The kinetics and thermodynamics of the chemical and physical processes that occur on the surface of a solid are greatly dependent on the structure of the surface. Few, if any surfaces are perfectly flat, and thus the cavities, protrusions, ridges, and edges of the surface must be treated differently when studying chemisorption and physisorption. Several types of spectroscopies and microscopies are available to study the atomic-scale structure of surfaces.

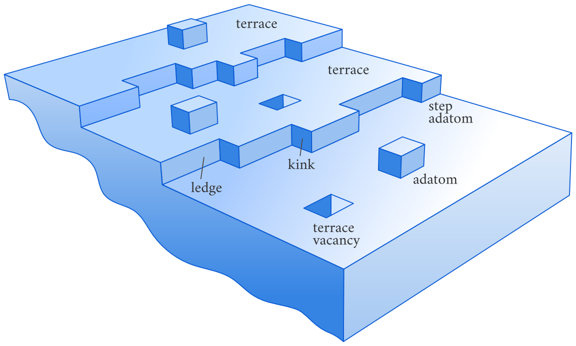


Figure 10.8.1: A schematic of a solid surface showing possible defects. The surface is composed of terraces, ledges, kinks, and steps. Terraces can contain adatoms (lone single atoms) and vacancies (missing atoms that leave cavities). (CC BY-NC; Ümit Kaya via LibreTexts)

10.8.1: Electron Microscopy

The two forms of electron microscopy which are commonly used to provide surface information are

- **Secondary Electron Microscopy** (SEM): which provides a direct image of the topographical nature of the surface from all the emitted secondary electrons
- **Scanning Auger Microscopy** (SAM): which provides compositional maps of a surface by forming an image from the Auger electrons emitted by a particular element.

Both techniques employ the focusing of the probe beam (a beam of high-energy electrons, typically 10 - 50 keV in energy) to obtain spatial localization.

10.8.1.1: Secondary Electron Microscopy (SEM)

As the primary electron beam is scanned across the surface, electrons of a wide range of energies will be emitted from the surface in the region where the beam is incident. These electrons will include backscattered primary electrons and Auger electrons, but the vast majority will be *secondary electrons* formed in multiple inelastic scattering processes (these are the electrons that contribute to the background and are completely ignored in Auger spectroscopy). The secondary electron current reaching the detector is recorded and the microscope image consists of a "plot" of this current, I, against probe position on the surface. The contrast in the micrograph arises from several mechanisms, but first and foremost from variations in the surface topography. Consequently, the secondary electron micrograph is virtually a direct image of the real surface structure (Figure $10.8.1$).

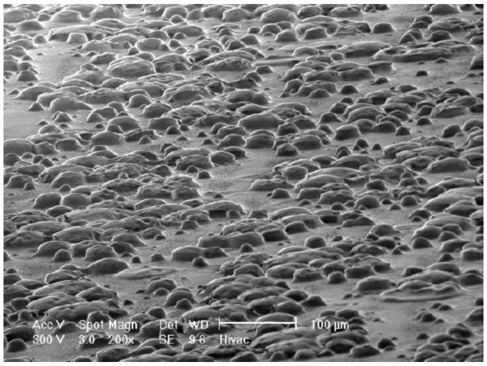


Figure 10.8.2: Low-voltage SEM micrograph (300 V) of distribution of adhesive droplets on a Post-it note. (CC BY-SA 3.0, Chivesud via Wikipedia)

The attainable resolution of the technique is limited by the minimum spot size that can be obtained with the incident electron beam, and ultimately by the scattering of this beam as it interacts with the substrate. With modern instruments, a resolution of better than 5 nm is achievable. This is more than adequate for imaging semiconductor device structures, for example, but insufficient to enable many supported metal catalysts to be studied in any detail.

10.8.1.2: Scanning Auger Microscopy (SAM)

The incident primary electrons cause the ionization of atoms within the region illuminated by the focused beam. Subsequent relaxation of the ionized atoms leads to the emission of Auger electrons characteristic of the elements present in this part of the sample surface. As with SEM , the attainable resolution is again ultimately limited by the incident beam characteristics. More significantly, however, the resolution is also limited by the need to acquire sufficient Auger signal to form a respectable image within a reasonable time period, and for this reason, the instrumental resolution achievable is rarely better than about 15-20 nm.

10.8.2: Low-Energy Electron Diffraction (LEED) Spectroscopy

LEED is the principal technique for the determination of surface structures. It may be used in one of two ways:

1. **Qualitatively**: where the diffraction pattern is recorded and analysis of the *spot positions* yields information on the size, symmetry, and rotational alignment of the adsorbate unit cell with respect to the substrate unit cell.
2. **Quantitatively**: where the *intensities* of the various diffracted beams are recorded as a function of the incident electron beam energy to generate so-called I-V curves which, by comparison with theoretical curves, may provide accurate information on atomic positions.

The LEED experiment uses a beam of electrons of a well-defined low energy (typically in the range 20 - 200 eV) incident normally on the sample. The sample itself must be a single crystal with a well-ordered surface structure in order to generate a back-scattered electron diffraction pattern. A typical experimental setup is shown in figure $10.8.3$below.

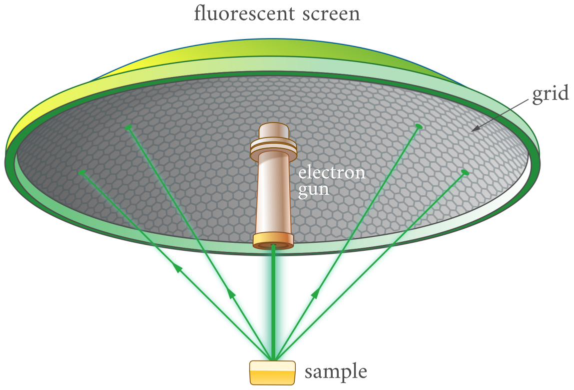


Figure 10.8.3: Schematic of a LEED experimental setup. (CC BY-NC; Ümit Kaya via LibreTexts)

Only the elastically-scattered electrons contribute to the diffraction pattern; the lower energy (secondary) electrons are removed by energy-filtering grids placed in front of the fluorescent screen that is employed to display the pattern.

Example 10.8.1

As shown by the Bragg equation, for the electrons to be diffracted, the de Broglie wavelength of the electrons has to be less than $2d$, which is twice the distance between the atomic planes. The equation used to calculate the wavelength (in nm) of backscattered electrons that are accelarated by a potential, ϕ is

$$\lambda = \left(\frac{1.504\, Vnm^2}{\phi}\right)^{1/2}$$

Calculate the minimum acceleration voltage needed to observe electron diffraction from the surface of a crystal with an interplanar spacing of 0.1250 nm.

Solution

To observe diffraction, the wavelength must be less than $2d$, so λ must be less than 0.2500 nm. Therefore,

$$0.2500\, nm = \left(\frac{1.504\, V nm^2}{\phi} \right)^{1/2}$$

$$\phi = \frac{1.504\, V nm^2}{(0.2500\, nm)^2}$$

$$\phi = 24.06 V$$

10.8.3: Contributors and Attributions

- Roger Nix (Queen Mary, University of London)

10.9: The Haber-Bosch Reaction Can Be Surface Catalyzed

10.9.1: The Haber-Bosch Process for Synthesis of Ammonia

An example of an industrial catalytic process is the Haber-Bosch process. Karl Bosch (1874–1940) was a German chemical engineer who was responsible for designing the process that took advantage of Fritz Haber's discoveries regarding the N_2 + H_2/NH_3 equilibrium to make ammonia synthesis via this route cost-effective. He received the Nobel Prize in Chemistry in 1931 for his work. The industrial process is called either the Haber process or the Haber-Bosch process. used to synthesize ammonia via the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

with

$$\Delta H_{rxn} = -91.8\ kJ/mol$$

Because the reaction converts 4 mol of gaseous reactants to only 2 mol of gaseous product, Le Chatelier's principle predicts that the formation of NH_3 will be favored when the pressure is increased. The reaction is exothermic, however (ΔH_{rxn} = −91.8 kJ/mol), so the equilibrium constant decreases with increasing temperature, which causes an equilibrium mixture to contain only relatively small amounts of ammonia at high temperatures ($10.9.1$). Taken together, these considerations suggest that the maximum yield of NH_3 will be obtained if the reaction is carried out at as low a temperature and as high a pressure as possible. Unfortunately, at temperatures less than approximately 300°C, where the equilibrium yield of ammonia would be relatively high, the reaction is too *slow* to be of any commercial use. The industrial process, therefore, uses a mixed oxide (Fe_2O_3/K_2O) catalyst that enables the reaction to proceed at a significant rate at temperatures of 400°C–530°C, where the formation of ammonia is less unfavorable than at higher temperatures.

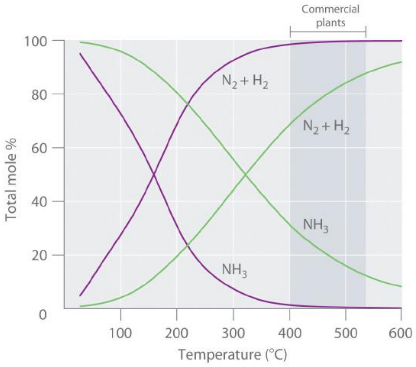


Figure $10.9.1$ Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen: At all temperatures, the total pressure in the systems was initially either 4 atm (purple curves) or 200 atm (green curves). Note the dramatic decrease in the proportion of NH_3 at equilibrium at higher temperatures in both cases, as well as the large increase in the proportion of NH_3 at equilibrium at any temperature for the system at higher pressure (green) versus lower pressure (purple). Commercial plants that use the Haber-Bosch process to synthesize ammonia on an industrial scale operate at temperatures of 400°C–530°C (indicated by the darker gray band) and total pressures of 130–330 atm.

Because of the low value of the equilibrium constant at high temperatures (e.g., K = 0.039 at 800 K), there is no way to produce an equilibrium mixture that contains large proportions of ammonia at high temperatures. We can, however, control the temperature and the pressure while using a catalyst to convert a fraction of the N_2 and H_2 in the reaction mixture to NH_3, as is done in the Haber-Bosch process. This process also makes use of the fact that the product—ammonia—is less volatile than the reactants. Because NH_3 is a liquid at room temperature at pressures greater than 10 atm, cooling the reaction mixture causes NH_3 to condense from the vapor as liquid ammonia, which is easily separated from unreacted N_2 and H_2. The unreacted gases are recycled until the complete conversion of hydrogen and nitrogen to ammonia is eventually achieved. Figure $10.9.2$ is a simplified layout of a Haber-Bosch process plant.

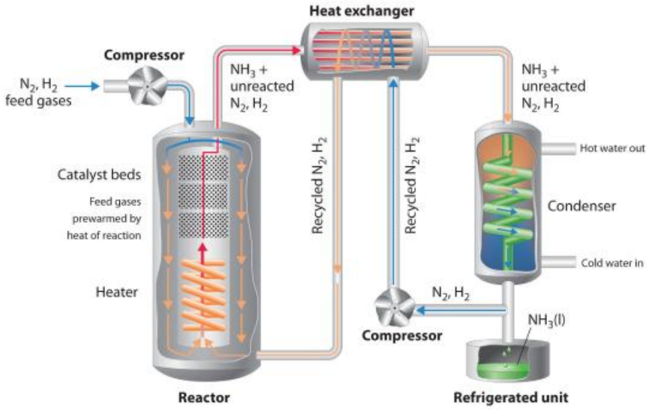


Figure 10.9.2 A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process: A 3:1 mixture of gaseous H_2 and N_2 is compressed to 130–330 atm, heated to 400°C–530°C, and passed over an Fe_2O_3/K_2O catalyst, which results in partial conversion to gaseous NH_3. The resulting mixture of gaseous NH_3, H_2, and N_2 is passed through a heat exchanger, which uses the hot gases to prewarm recycled N_2 and H_2, and a condenser to cool the NH_3, giving a liquid that is readily separated from unreacted N_2 and H_2. (Although the normal boiling point of NH_3 is −33°C, the boiling point increases rapidly with increasing pressure, to 20°C at 8.5 atm and 126°C at 100 atm.) The unreacted N_2 and H_2 are recycled to form more NH_3.

We can write the seven reactions that are involved in the process where ad indicates that the molecule or atom is adsorbed on the catalyst

$$H_2(g) + 2S(s) \rightleftharpoons 2H(ad) \tag{10.9.1}$$

$$N_2(g) \rightleftharpoons N_2(ad) \tag{10.9.2}$$

$$N_2(ad) + 2S(s) \rightleftharpoons 2N(ad) \tag{10.9.3}$$

$$H(ad) + N(ad) \rightleftharpoons NH(ad) \tag{10.9.4}$$

$$NH(ad) + H(ad) \rightleftharpoons NH_2(ad) \tag{10.9.5}$$

$$NH_2(ad) + H(ad) \rightleftharpoons NH_3(ad) \tag{10.9.6}$$

$$NH_3(ad) \rightleftharpoons NH_3(g) \tag{10.9.7}$$

Reaction 10.9.3 is much the slowest, and therefore the rate determining step. Figure 10.9.3 summarizes the reaction scheme.

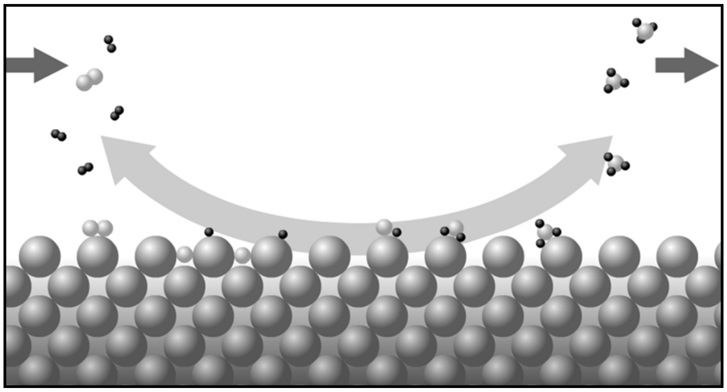


Figure 10.9.3: A representation of the reactions Eqs. 10.9.1 to 10.9.7 with H_2 and N_2 coming in from the left and being adsorbed on the catalyst. The H_2 and N_2 then atomize on the surface of the catalyst, followed by a set of sequential reactions forming NH, NH_2 and finally NH_3 which desorbs from the catalyst as shown on the right

Gerhard Ertl worked out the energetics of the reaction shown in Figure 10.9.4 below shows the amount of energy per mole needed on the catalyst and that which would be needed in the gas phase. Ertl's Nobel Prize speech about his work on the catalytic reactions forming ammonia and other catalytic reactions can be viewed on line.

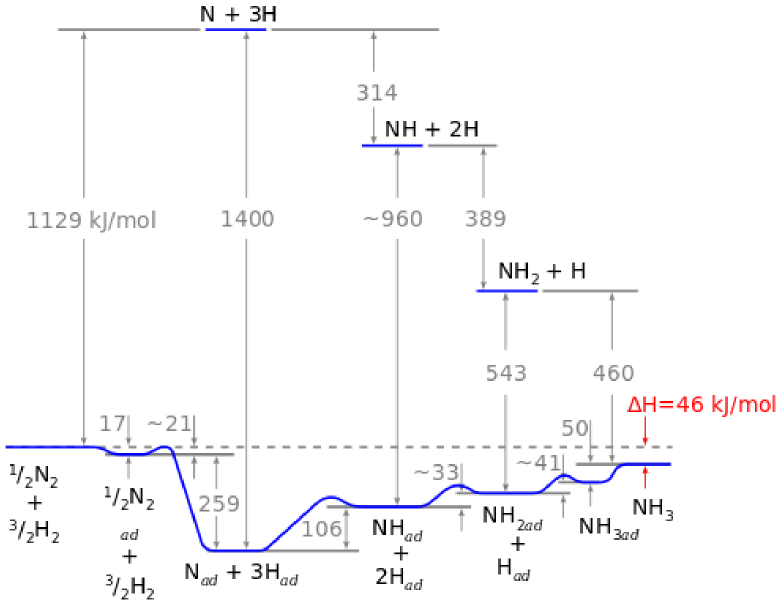


Figure 10.9.4: Ertl's group was able to measure the energy needed for each step of the Bosch-Haber process as opposed to the energy that would be needed in the gas phase.

Further studies of the Fe_2O_3/K_2O catalyst have shown that the rate of the reaction depends on the particular surface on which the reaction is occurring. Figure 10.9.5 shows the reaction rates for the synthesis of ammonia on five different surfaces of the iron.

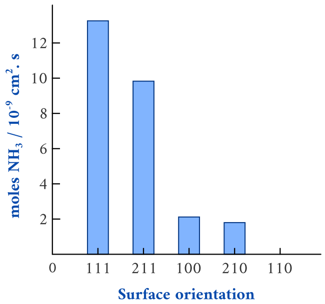


Figure 10.9.5: The rates of ammonia production for various iron catalyst surfaces. (CC BY-NC; Ümit Kaya via LibreTexts)

10.9.1.1: Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

Figure 10.9.3 is from the ESA, now available on the internet wayback machine

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10.10: Fluorescence

Fluorescence, a type of luminescence, occurs in gas, liquid or solid chemical systems. Fluorescence is brought about by absorption of photons in the singlet ground state promoted to a singlet excited state. The spin of the electron is still paired with the ground state electron, unlike phosphorescence. As the excited molecule returns to ground state, it involves the emission of a photon of lower energy, which corresponds to a longer wavelength, than the absorbed photon.

Introduction

The energy loss is due to vibrational relaxation while in the excited state. Fluorescent bands center at wavelengths longer than the resonance line. This shift toward longer wavelengths is called a Stokes shift. Excited states are short-lived with a lifetime at about 10^{-8} seconds. Molecular structure and chemical environment affect whether or not a substance luminesces. When luminescence does occur, molecular structure and chemical environment determine the intensity of emission. Generally molecules that fluoresce are conjugated systems. Fluorescence occurs when an atom or molecules relaxes through vibrational relaxation to its ground state after being electrically excited. The specific frequencies of excitation and emission are dependent on the molecule or atom.

$$S_0 + h\nu_{ex} = S_1 \tag{10.10.1}$$

where

- $h\nu$ is a photon energy with
- h is Planck's constant and
- ν is the frequency of light,
- S_0 is the ground state of the fluorophore and
- S_1 is its first electronically excited state.

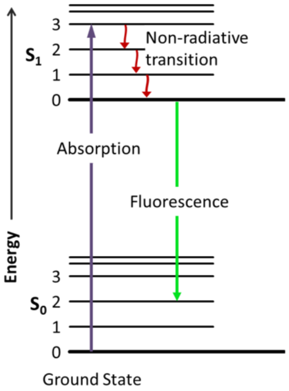

Figure 1: Jablonski diagram of absorbance, non-radiative decay, and fluorescence. (Public Domain, Jacobkhed)

Figure 1 is a Jablonski energy diagram representing fluorescence. The purple arrow represents the absorption of light. The green arrow represents vibrational relaxation from singlet excited state, S_2 to S_1. This process is a non-radiative relaxation in which the excitation energy is dispersed as vibrations or heat to the solvent, and no photon is emitted. The yellow arrow represents fluorescence to the singlet ground state, S_o.

The fluorescence quantum yield ((\Phi\)) gives the efficiency of the fluorescence process. It is the ratio of photons emitted to photons absorbed.

$$\Phi = \frac{\#\text{ emitted photons}}{\#\text{ absorbed photons}} \tag{10.10.2}$$

If every photon absorbed results in a photon emitted. The maximum fluorescence quantum yield is 1.0, and compounds with quantum yields of 0.10 are still considered fluorescent. Another way to define the fluorescence quantum yield is by the excited state decay rates:

$$\Phi = \frac{k_f}{\sum_i k_i} \tag{10.10.3}$$

where k_f is the rate of spontaneous emission of radiation and the denominator is the sum of all rates of excited state decay for each deactivation process (ie phosphorescence, intersystem crossing, internal conversion…). The fluorescence lifetime is the average time the molecule remains in its excited state before emitting a photon. Fluorescence typically follows first-order kinetics:

$$[S_1] = [S_1]_o e^{-t/\tau} \tag{10.10.4}$$

where

- $[S_1]$ is the concentration of excited state molecules at time t,
- $[S_1]_0$ is the initial concentration and τ is the decay rate.

Various radiative and non-radiative processes can de-populate the excited state so the total decay rate is the sum over all rates:

$$\tau_{tot} = \tau_{rad} + \tau_{nrad} \tag{10.10.5}$$

where τ_{tot} is the total decay rate, τ_{rad} the radiative decay rate and τ_{nrad} the non-radiative decay rate. If the rate of spontaneous emission or any of the other rates are fast, the lifetime is short. The average lifetime of fluorescent compounds that emit photons with energies from the UV to near infrared are within the range of 0.5 to 20 nanoseconds.

The fluorescence intensity, I_F is proportional to the amount of light absorbed and the fluorescence quantum yield, Φ

$$I_f = kI_o\phi[1-(10^{-\varepsilon bc})] \tag{10.10.6}$$

where

- k is a proportionality constant attributed to the instrument
- \(I_o\(is the incident light intensity
- ϵ is the molar absorptivity,
- b is the path length, and
- c is the concentration of the substrate.

If dilute solutions are used so that less than 2% of the excitation energy is absorbed, then an approximation can be made so that

$$10^x \approx 1 + x + \dots \tag{10.10.7}$$

so Equation 10.10.6can be simplified to

$$I_f = kI_o\Phi[\varepsilon bc] \tag{10.10.8}$$

This relationship shows that fluorescence intensity is **proportional** to concentration.

Fluorescence rarely results from absorption of UV-radiation of wavelengths shorter than 250 nm because this type of radiation is sufficiently energetic to cause deactivation of the excited state by predissociation or dissociation. Most organic molecules have at least some bonds that can be ruptured by energies of this strength. Consequently, fluorescence due to $sigma^* \rightarrow \sigma$ transitions is rarely observed. Instead such emission is confined to the less energetic $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow n$ processes. Fluorescence commonly occurs from a transition from the lowest vibrational level of the first excited electronic state to the one of the vibrational levels of the electronic ground state. Quantum yield (Φ) is greater for $\pi^* \rightarrow \pi$ transition because these excited states show short average lifetimes (larger k_f) and because deactivation processes that compete with fluorescence is not as likely to happen. Molar absorptivity of π → π* transitions is 100-1000 fold greater. The average lifetime is 10^{-7} to 10^{-9} seconds for ?, ?* states and 10^{-5} to 10^{-7} seconds for n, π* states.

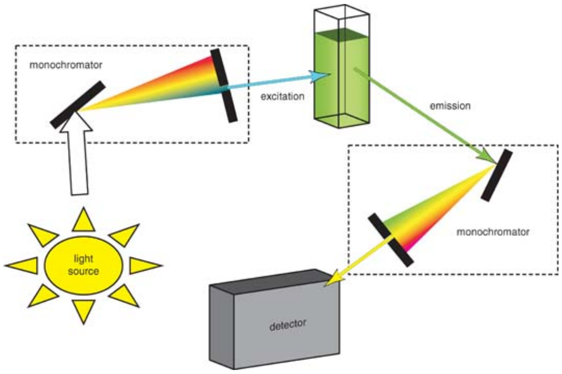

Figure 2: Schematic representation of a fluorescence spectrometer. from OpenStax (CC-BY-3.0)

Figure 2 is a schematic of a typical filter fluorometer that uses a source beam for fluorescence excitation and a pair of photomultiplier tubes as transducers. The source beam is split near the source into a reference beam and a sample beam. The reference beam is attenuated by the aperture disk so that its intensity is roughly the same as the fluorescence intensity. Both beams pass through the primary filter, with the reference beam being reflected to the reference photomultiplier tube. The sample beam is focused on the sample by a pair of lenses and causes fluorescence emission. The emitted radiation passes through a second filter and then is focused on the sample photomultiplier tube. The electrical outputs from the two transducers are then processed by an analog to digital converter to compute the ratio of the sample to reference intensities, which can then be used for qualitative and quantitative analysis. To obtain an emission spectrum, the excitation monochromator is fixed and the emission monochromator varies. To obtain an excitation spectrum, the excitation monochromator varies while the emission monochromator is fixed.

Fluorescence spectroscopy can be used to measure the concentration of a compound because the fluorescence intensity is linearly proportional to the concentration of the fluorescent molecule. Fluorescent molecules can also be used as tags. For example, fluorescence in situ hybridization (FISH) is a method of determining what genes are present in an organism's genome. Single stranded DNA encoding a gene of interest is covalently bonded to a fluorescent molecule and washed over the organism's chromosome, binding to its complementary sequence. The presence and placement of the gene in the organism then fluoresces when shined with ultraviolet light. Green fluorescence protein (GFP) is used in molecular biology to monitor the activity of proteins. The gene encoding GFP can be inserted next to a gene encoding a protein that will be studied. When the genes are expressed, the protein will be attached to GFP and can be identified in the cell by its fluorescence.

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