

Chapter 1

Gases

We spent last semester learning about the structure and behavior of individual molecules. This semester will be spent learning about the behavior of collections of molecules. We'll start with gases, where the molecules more or less act individually.

1.1 Kinetic-molecular theory of gases

The “kinetic theory of gases” makes the following assumptions about gases:

1. Gases are composed of particles in constant, random motion.
2. The particles are negligibly small compared to the distances between them and the size of the container.
3. The particles do not interact except that they have collisions with each other and the container walls. In these collisions, the average translational energy is conserved.
4. The particles move according to classical mechanics.

All but the first of those assumptions are not strictly true, so we should expect the theory to disagree with observation in some circumstances. We'll have to see whether the disagreements are frequent enough to cause trouble.

1.1.1 Pressure of an ideal gas

Consider a gas of identical molecules in a cubical container with sides of length l . We want to calculate from kinetic theory the pressure the gas exerts on the walls.

Pressure is force per unit area, so we will calculate the force on one wall of the box and divide by its area l^2 . From elementary mechanics we have

$$F = ma = m \frac{dv}{dt} = \frac{d(mv)}{dt} = \frac{dp}{dt}, \quad (1.1)$$

so we will evaluate the force as $\frac{\Delta p}{\Delta t}$ from the momentum change Δp at the wall during some time interval Δt .

First imagine a single gas molecule in the box. The components of its velocity are v_x , v_y , and v_z . Its speed is $v = (v_x^2 + v_y^2 + v_z^2)^{\frac{1}{2}}$, and its translational energy is $\epsilon_{\text{tr}} = \frac{1}{2} m v^2$, where m is the molecule's mass. The x component of its momentum is $m v_x$. When the molecule collides with a wall parallel to the yz plane, let us assume that the x component of its velocity changes sign, and the other two components are unaffected. (This assumption is not necessarily true for a single molecule having a single collision, but it must be true on average, or else the gas could develop a net direction of travel inside the box.) The change in momentum of the particle is therefore $\Delta p = 2 m v_x$. The molecule will bounce back and forth in the box (possibly also moving in the y and z directions, but those do not affect the x motion). The round-trip time in the x direction is $\Delta t = 2l / v_x$, so the average force must be $F = \frac{\Delta p}{\Delta t} = \frac{2 m v_x}{2l / v_x} = \frac{m v_x^2}{l}$. The pressure this one-molecule gas exerts on the wall is then $F/A = F/l^2 = m v_x^2 / l^3 = m v_x^2 / V$. For the one-molecule gas we therefore have $PV = m v_x^2$.

If we have N molecules that don't interact, their forces on the wall (since they are all in the same direction) simply add, and we have

$$PV = \sum_{i=1}^N m v_{xi}^2 = m N \frac{\sum_{i=1}^N v_{xi}^2}{N} = m N \langle v_x^2 \rangle, \quad (1.2)$$

where the angle brackets indicate the usual average (add up the individual values of v_x^2 and divide by the number of molecules.)

There is nothing special about the x direction, so we expect that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$. The square of the speed of a molecule is $v^2 = v_x^2 + v_y^2 + v_z^2$, so the average squared speed is

$$\langle v^2 \rangle = \frac{1}{N} \sum_{i=1}^N (v_{xi}^2 + v_{yi}^2 + v_{zi}^2) \quad (1.3)$$

$$= \frac{1}{N} \left[\sum_{i=1}^N (v_{xi}^2) + \sum_{i=1}^N (v_{yi}^2) + \sum_{i=1}^N (v_{zi}^2) \right] \quad (1.4)$$

$$= \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \quad (1.5)$$

$$\langle v^2 \rangle = 3 \langle v_x^2 \rangle \quad (1.6)$$

so $\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$. Substituting into Eq. (1.2) gives

$$PV = \frac{1}{3} mN \langle v^2 \rangle = \frac{1}{3} nM \langle v^2 \rangle, \quad (1.7)$$

where n is the number of moles and M is the molar mass. This formula gives the pressure of the gas in terms of microscopic properties of the molecules (their masses and average squared speed). We see that the pressure is directly related to the average of the squared speed of the gas molecules: the faster they go, the higher the pressure.

1.1.2 RMS speed and average translational energy

The ideal gas law is $PV = nRT = Nk_B T$, where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. From that we immediately obtain a formula for the average squared speed:

$$\langle v^2 \rangle = \frac{3RT}{M} = \frac{3k_B T}{m}. \quad (1.8)$$

The “root-mean-square” or RMS speed c is just the square root of the average squared speed, and gives a measure of the typical speed of molecules in a sample of gas:

$$c = \sqrt{\langle v^2 \rangle} = \left(\frac{3k_B T}{m} \right)^{\frac{1}{2}} = \left(\frac{3RT}{M} \right)^{\frac{1}{2}}. \quad (1.9)$$

In problems the second form is more convenient, but you must remember to put in the molar mass M in kg/mol.

Example What is the RMS speed of a N_2 molecule at 300 K? We have

$$c = \left(\frac{3RT}{M} \right)^{\frac{1}{2}} = \left(\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{0.028 \text{ kg mol}^{-1}} \right)^{\frac{1}{2}} = 517 \text{ m/s}.$$

1.1.3 Average speed, translational energy, and temperature

By arguments similar to Eq. (1.3), you can show that the average translational energy per molecule is $\langle \epsilon_{\text{tr}} \rangle = \frac{1}{2} m \langle v^2 \rangle$, so from Eq. (1.8) we find immediately

$$\langle \epsilon_{\text{tr}} \rangle = \frac{3}{2} k_B T. \quad (1.10)$$

So the average translational energy in a gas is indeed proportional to the absolute temperature, and now we know the proportionality constant.

For the whole sample of N particles we have $E_{\text{tr}} = \frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT$. It is important to notice that even though the molecules have a wide distribution of speeds (more on that later), the translational energy of the whole sample is very well defined if N is large. Substituting PV from the ideal gas law gives

$$PV = \frac{2}{3}N\langle\epsilon_{\text{tr}}\rangle = \frac{2}{3}E_{\text{tr}}. \quad (1.11)$$

1.1.4 The distribution of speeds

The molecules do not all move with the same speed. To describe the distribution of speeds, we need to use a probability density function, just as in quantum mechanics (where the probability density function, ψ^2 , described the distribution of position). Remarkably, we can find the distribution of speeds assuming only that all directions in space are equivalent, and that the different velocity components for a molecule are independent: what a molecule's speed is in the x direction says nothing about its speed in the y or z directions.

One-dimensional velocity distribution

First, let's seek the one-dimensional distribution of speeds, $f(v_x)$, such that the fraction of molecules with x -components of speed between a and b is

$$P(a \leq v_x \leq b) = \int_a^b f(v_x) dv_x \quad (1.12)$$

Because all directions in space are equivalent, the function of $f(v_x)$ must be the same one that describes the probability distributions in v_y and v_z as well. You can think of this one-dimensional function of v_x as giving the probability that a molecule will have its x component of velocity between v_x and $v_x + dv_x$.

The probability density must be normalized, so that

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1 \quad (1.13)$$

Now, what is the probability that a particular molecule will have its x component of velocity between v_x and $v_x + dv_x$, its y component of velocity between v_y and $v_y + dv_y$, and its z component of velocity between v_z and $v_z + dv_z$? Because the speeds in the various directions are assumed to be independent, that must be the *product* of the three one-dimensional probabilities:

$$\frac{dN_{v_x v_y v_z}}{N} = f(v_x)f(v_y)f(v_z) dv_x dv_y dv_z \quad (1.14)$$

This is a three-dimensional function, of velocity. But, by the assumption of equivalence of directions, it cannot depend on the direction of the velocity; it can only depend on speed. Therefore,

$$f(v_x)f(v_y)f(v_z) = \phi(v) \quad (1.15)$$

a function of speed only ($v^2 = v_x^2 + v_y^2 + v_z^2$). Now, what kind of function satisfies this requirement, that a product of functions of different arguments is equal to a single function of the sum of the arguments? There's only one function that does that: the exponential, because $e^a e^b e^c = e^{a+b+c}$. In this case a must be v_x^2 and so on, so the candidate function is

$$f(v_x) = Ae^{-\frac{1}{2}bv_x^2}, \quad (1.16)$$

a Gaussian! I have inserted the $-\frac{1}{2}$ for later convenience (this only changes the definition of b .) A and b are yet to be determined, but if we choose this distribution function, we can be assured that the requirements of our assumptions will be satisfied.

To find A , we normalize: the particle must have some x component of velocity, between $-\infty$ and ∞ . So

$$\int_{-\infty}^{\infty} Ae^{-\frac{1}{2}bv_x^2} dv_x = 1 \quad (1.17)$$

We can do this using the standard integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad (1.18)$$

where $a > 0$, so that

$$A \left(\frac{2\pi}{b} \right)^{\frac{1}{2}} = 1 \quad (1.19)$$

$$A = \left(\frac{b}{2\pi} \right)^{\frac{1}{2}} \quad (1.20)$$

Notice that b must be positive for this normalization to work; otherwise the integral is infinite and our function is not an acceptable probability density.

Now we need to find b . We have $\langle v^2 \rangle = 3\langle v_x^2 \rangle = 3kT/m$, so that $\langle v_x^2 \rangle = kT/m$. We can also calculate that average from the probability density function, using the usual formula for the average of a function:

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x) dv_x \quad (1.21)$$

$$= \left(\frac{b}{2\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} v_x^2 e^{-\frac{1}{2}bv_x^2} dv_x \quad (1.22)$$

We need the standard integral

$$\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx = \frac{(2n)! \pi^{\frac{1}{2}}}{2^{2n} n! a^{n+1/2}}, \quad (1.23)$$

which with $n = 1$ and $a = b/2$ gives us

$$\langle v_x^2 \rangle = \left(\frac{b}{2\pi} \right)^{\frac{1}{2}} \frac{2! \pi^{\frac{1}{2}}}{2^2 (b/2)^{3/2}} \quad (1.24)$$

$$= \frac{1}{b} \quad (1.25)$$

so we now have

$$b = (\langle v_x^2 \rangle)^{-1} \quad (1.26)$$

$$= \left(\frac{k_B T}{m} \right)^{-1} \quad (1.27)$$

$$= \frac{m}{k_B T} \quad (1.28)$$

so that finally

$$f(v_x) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} \exp\left(-\frac{m v_x^2}{2k_B T} \right). \quad (1.29)$$

This expression gives us the one-dimensional distribution of velocity. Examples are plotted in Figure 1.1.

Any particular molecule could have a velocity component (or projection) along the x axis anywhere between $-\infty$ and ∞ ; this distribution function shows us that the most likely velocity component is zero, and that the probability density falls off with increasing $|v_x|$ in a Gaussian way. Note that the Gaussian will be wider for larger T and for smaller m . Also note that the average speed along the x -axis is zero: there is no net tendency for the molecules to be moving either left or right. (That is why we had to evaluate b using $\langle v_x^2 \rangle$ rather than $\langle v_x \rangle$; the latter quantity is zero no matter what value b has.)

Notice that the one-dimensional distribution can be written

$$f(v_x) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} \exp\left(-\frac{\varepsilon_{\text{tr},x}}{k_B T} \right). \quad (1.30)$$

The argument of the exponential is the ratio of two terms, each with dimensions of energy: the “one-dimensional translational energy” of the molecule, $\varepsilon_{\text{tr},x}$, and the “characteristic energy” kT . It is relatively easy for molecules to have translational energies less than or similar to kT , while it is quite improbable that they will have energies much greater than kT . This is our first example of the extremely important Boltzmann distribution.

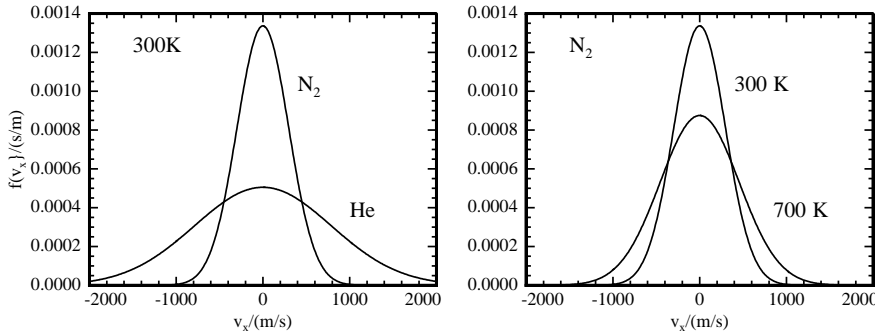


Figure 1.1: The one-dimensional velocity distribution, showing variations with molecular mass and with temperature. The area under each curve is 1.

Three-dimensional speed distribution

Now we want to go on to find the distribution of molecular speeds in three dimensions. Note that while the velocity component v_x in a single dimension can have any value between $-\infty$ and ∞ , the speed of a molecule is a necessarily positive quantity, because $v^2 = v_x^2 + v_y^2 + v_z^2$. We will therefore expect to find a probability density function $F(v)$ that is nonzero only for positive v .

Eq. (1.14) gave the probability that a molecule has its x -component of velocity between v_x and $v_x + dv_x$, y -component of velocity between v_y and $v_y + dv_y$, and its z -component of velocity between v_z and $v_z + dv_z$, as the product of the three independent probabilities. (Think of the probability of three people simultaneously flipping coins all getting heads: it's $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$.) That is,

$$\frac{dN_{v_x v_y v_z}}{N} = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T} \right) dv_x dv_y dv_z \quad (1.31)$$

(Notice that the exponent on the normalization factor is now 3/2.) If you think of the function $dN_{v_x v_y v_z}/N$ as living in a three-dimensional “velocity space” whose axes are v_x , v_y , and v_z , then the $dv_x dv_y dv_z$ part of Eq. (1.31) describes the volume of a small rectangular box, which is located a distance v from the origin. We are looking for a distribution in speed only, and we don't care what direction the molecule is moving. The most straightforward way to find that distribution is to convert Eq. (1.31) to the spherical polar coordinates v, θ, ϕ . The two angles specify the direction of motion and the v variable (which corresponds to r in

ordinary spatial coordinates) is exactly the speed variable we are interested in. We can then integrate over the angular coordinates θ and ϕ .

To change the distribution to spherical polar coordinates, we use the substitution $v^2 = v_x^2 + v_y^2 + v_z^2$, and we must also remember to convert the “volume element” $dx dy dz$ to the spherical polar element $v^2 \sin \theta dv d\theta d\phi$. We then integrate over the angles:

$$F(v)dv = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \exp\left(-\frac{mv^2}{2k_B T}\right) v^2 dv \quad (1.32)$$

The only angular dependence is the simple $\sin \theta$, so the integration over both θ and ϕ is easy and just gives 4π . So our final distribution of molecular speeds is

$$F(v) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \quad (1.33)$$

Eq. (1.33) is called the *Maxwell distribution of speeds*.

I think of this distribution in three parts: there’s a normalization part, a $4\pi v^2$ part that counts all the possible *velocities* that correspond to the same *speed*, and there is an exponential “Boltzmann factor” that compares the kinetic energy of the molecule to kT , the average energy available at temperature T .

What do these curves look like? The normalization part does not depend on v ; the v^2 part is a parabola; the Boltzmann part is a Gaussian centered at zero. So at low speeds the curve looks like a rising parabola, then as v^2 increases the curve turns over and dives back into the baseline as the Gaussian becomes small. Figure 1.2 shows examples corresponding to the 1D distributions we saw before.

1.1.5 Testing the Maxwell distribution

I know of two good methods for experimentally checking the Maxwell distribution of speeds: time-of-flight methods, including the use of slotted-disk “velocity selectors”, probably described in your textbook, and Doppler spectroscopy.

In a velocity selector experiment, molecules leave a source through a small hole, and then pass through a series of disks with slots in them. The disks are arranged on a rotating shaft and the slots are offset, so that for a particular speed of rotation only molecules of a particular speed can make it through all the slots. Which speed makes it through is controlled by the rotation rate of the shaft. These experiments were first done by Eldridge in 1927 (J. A. Eldridge, *Phys. Rev.* **30**, 931 (1927).) A thorough analysis of slotted-disk velocity selectors by C. J. B. van den Meijdenberg appears in *Atomic and Molecular Beam Methods*, G. Scoles, ed., (Oxford, 1988).

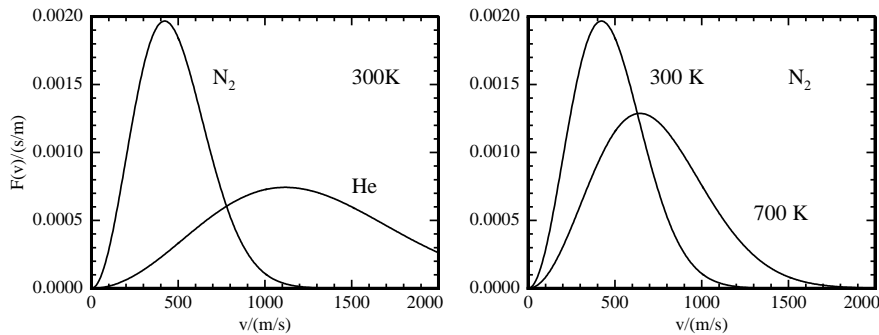


Figure 1.2: The Maxwell distribution of speeds. The area under each of the curves is 1.

In Doppler spectroscopy, the absorption spectrum of gas molecules is measured with very high resolution. Nowadays such spectroscopy is often done with lasers since they can provide the required resolution easily. A molecule moving toward a laser source will “see” a frequency that is higher than the frequency of the laser because of the Doppler effect. The shift is proportional to v_x/c , where v_x is the component of the molecule’s velocity along the laser beam direction and c is the speed of light. The absorption spectrum that appears therefore has lines that are broadened by the motion of the molecules, and if the line shape is measured carefully, the distribution $f(v_x)$ can be determined directly.

1.1.6 Applications of the Maxwell distribution

Average speed $\langle v \rangle$

We use the usual approach to averaging things:

$$\langle v \rangle = \int_0^{\infty} v F(v) dv \quad (1.34)$$

$$= \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} 4\pi \int_0^{\infty} v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv \quad (1.35)$$

Use the standard integral

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \quad (1.36)$$

with $n = 1$ and $a = \frac{m}{2kT}$ to give

$$\langle v \rangle = \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} 4\pi \frac{1!}{2 \left(\frac{m}{2kT} \right)^2} \quad (1.37)$$

$$= \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}} \quad (1.38)$$

The average speed $\langle v \rangle$ differs from the root-mean-square speed $\sqrt{\langle v^2 \rangle} = c$ because it contains the numerical factor $\sqrt{8/\pi} = \sqrt{2.546}$ rather than $\sqrt{3}$.

Most probable speed v_{mp}

The most probable speed is the speed at which $F(v)$ reaches a maximum. We find it by differentiating $F(v)$, setting the derivative equal to 0, and solving for v_{mp} ; I ask you to work it out in a homework problem. The result is

$$v_{\text{mp}} = \left(\frac{2k_B T}{m} \right)^{\frac{1}{2}} \quad (1.39)$$

The most probable speed has $\sqrt{2}$ as the numerical factor multiplying $\left(\frac{kT}{m} \right)^{\frac{1}{2}}$; it is the smallest of the three measures of speed we have considered.

Wall collision rates and effusion

Collision rate with a wall Let's work out the number of molecules that hit a container wall in a time Δt . We'll do this by considering the contribution of each velocity separately, then adding them up, using the same cubical box of side l we used before.

Let's say the wall is perpendicular to the x axis. The number of molecules in the gas with x component of velocity between v_x and $v_x + dv_x$ is just $Nf(v_x)dv_x$, where $f(v_x)$ is the one-dimensional velocity distribution and N is the total number of molecules. Those molecules will hit the wall in time Δt if v_x is *toward* the wall and they start out within a distance $v_x \Delta t$ of the wall. Since the length of the box is l , the fraction of those molecules close enough to hit the wall is $v_x \Delta t / l$, so the number of collisions they contribute is $(v_x \Delta t / l) N f(v_x) dv_x$. The total number of wall collisions during time Δt is the sum of the contributions from all velocities, or

$$N_{\text{wall}} = \frac{N \Delta t}{l} \int_0^{\infty} v_x f(v_x) dv_x. \quad (1.40)$$

Notice that we only integrate from 0 up to ∞ , not from $-\infty$; molecules that are moving *away* from the wall don't hit it. Putting in Eq. (1.29) for $f(v_x)$ we have

$$N_{\text{wall}} = \frac{N\Delta t}{l} \left(\frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} \int_0^{\infty} v_x \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x. \quad (1.41)$$

The integral can be done with straightforward substitution and equals $k_B T/m$, so we have

$$N_{\text{wall}} = \frac{N\Delta t}{l} \left(\frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} \frac{k_B T}{m} = \frac{N\Delta t}{l} \left(\frac{k_B T}{2\pi m} \right)^{\frac{1}{2}}. \quad (1.42)$$

A more generally useful quantity is the collision rate per unit area, which is simply $\frac{N_{\text{wall}}}{l^2 \Delta t}$; since $l^3 = V$, that rate is

$$\frac{1}{A} \frac{dN_{\text{wall}}}{dt} = \frac{1}{4} \frac{N}{V} \langle v \rangle = \frac{1}{4} \frac{PN_A}{RT} \langle v \rangle \quad (1.43)$$

where N_A is Avogadro's number, and we have used the ideal gas law and $\langle v \rangle = \sqrt{8k_B T/\pi m}$. So the number of collisions per second with a wall is proportional to P and to $\langle v \rangle$, as we expected.

Effusion rates Now, say we punch a small hole in the wall of area a , and we put the box in a vacuum system so there is no gas to leak into the container. This hole must be small enough that leaks through it don't disturb the distribution of speeds or densities in the main gas; effectively, the molecules must escape one at a time. At what rate does gas leak out? Each molecule that hits the hole will escape, so the escape rate will be just the area of the hole times the collision frequency. The rate of change of the number of molecules N in the container will be just

$$\frac{dN}{dt} = -\frac{aPN_A}{4RT} \langle v \rangle = \frac{-aPN_A}{(2\pi MRT)^{1/2}}. \quad (1.44)$$

Effusion from a mixture of gases can be used to separate the gas molecules by mass. The effusion rate is proportional to the inverse square root of the molecular mass; light molecules escape through the hole more quickly than heavier ones. The effusing gas is therefore enriched in the light component. This effect is the basis of the gaseous-diffusion technique used at Oak Ridge to separate uranium isotopes for the first atomic bombs.

It is convenient to rewrite Eq. (1.44) in terms of mass. Converting the number of molecules N to the mass by dividing by Avogadro's number and multiplying by the molecular weight M , we find for the rate of mass loss

$$\frac{dm_{\text{gas}}}{dt} = -aP \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}} \quad (1.45)$$

This expression provides a standard way of determining the vapor pressures of not-very-volatile substances. If you put a sample of solid inside a cell with a small hole of known area a (determined with a microscope), apply a vacuum pump to the other side of the hole, let the material effuse for a while (typically minutes to hours), and then measure the loss of mass of your sample, you can determine its vapor pressure P . Irving Langmuir at General Electric measured vapor pressure curves for tungsten this way more than fifty years ago, and his results still appear in standard reference books; they have not been improved upon.

1.1.7 Translational energy distribution

Let's consider the Maxwell distribution in terms of translational energy rather than speed. We need to make a change of variable. Any time you convert a *distribution* from one set of variables to another, you must be careful: you must make sure that probabilities calculated from the distributions written in terms of the two different variables match up. In other words, if the energy distribution is $G(\varepsilon_{\text{tr}})$, we must have $G(\varepsilon_{\text{tr}}) d\varepsilon_{\text{tr}} = F(v) dv$. Therefore, we must be careful to change variables in the accompanying differential dv as well as in $F(v)$ itself. When we converted the Maxwell distribution from Cartesian to spherical polar coordinates above, we did this matching "automatically" by knowing beforehand that the new volume element in spherical polar coordinates was $r^2 \sin\theta dr d\theta d\phi$. Here we are making a different change so I will show the conversion in more detail.

We want to change from v to ε_{tr} , starting from

$$G(\varepsilon_{\text{tr}}) d\varepsilon_{\text{tr}} = F(v) dv \quad (1.46)$$

$$G(\varepsilon_{\text{tr}}) d\varepsilon_{\text{tr}} = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv \quad (1.47)$$

We have $\varepsilon_{\text{tr}} = \frac{1}{2}mv^2$, so $v = \left(\frac{2\varepsilon_{\text{tr}}}{m}\right)^{\frac{1}{2}}$ and $dv = \frac{1}{2}\left(\frac{2\varepsilon_{\text{tr}}}{m}\right)^{-\frac{1}{2}} \frac{2}{m} d\varepsilon_{\text{tr}} = \left(\frac{1}{2m\varepsilon_{\text{tr}}}\right)^{\frac{1}{2}} d\varepsilon_{\text{tr}}$. In the Maxwell distribution $F(v) dv$, we replace v with $\left(\frac{2\varepsilon_{\text{tr}}}{m}\right)^{\frac{1}{2}}$ and dv with $\left(\frac{1}{2m\varepsilon_{\text{tr}}}\right)^{\frac{1}{2}} d\varepsilon_{\text{tr}}$ to get

$$G(\varepsilon_{\text{tr}}) d\varepsilon_{\text{tr}} = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi \left(\frac{2\varepsilon_{\text{tr}}}{m}\right) \exp\left(-\frac{\varepsilon_{\text{tr}}}{k_B T}\right) \left(\frac{1}{2m}\right)^{\frac{1}{2}} \varepsilon_{\text{tr}}^{-\frac{1}{2}} d\varepsilon_{\text{tr}} \quad (1.48)$$

$$= 2\pi \left(\frac{1}{\pi k_B T}\right)^{\frac{3}{2}} \varepsilon_{\text{tr}}^{\frac{1}{2}} \exp\left(-\frac{\varepsilon_{\text{tr}}}{k_B T}\right) d\varepsilon_{\text{tr}} \quad (1.49)$$

so we say that

$$G(\epsilon_{\text{tr}}) = 2\pi \left(\frac{1}{\pi k_{\text{B}} T} \right)^{\frac{3}{2}} \epsilon_{\text{tr}}^{\frac{1}{2}} \exp\left(-\frac{\epsilon_{\text{tr}}}{k_{\text{B}} T}\right). \quad (1.50)$$

All the dependence on mass has canceled; the translational energy distribution is the same for all molecules at the same temperature. Figure 1.3 shows this distribution for temperatures of 300 and 700 K.

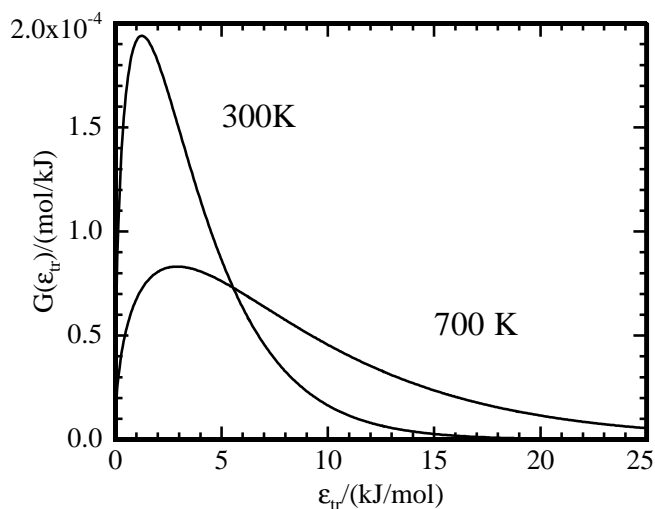


Figure 1.3: Translational energy distributions for gases. The distribution is independent of mass.

The translational energy distribution rises very steeply from the origin; it has infinite slope at the origin, while the speed distribution has zero slope there. If you draw a vertical line at any energy, the area under the distribution to the right of that line gives the fraction of molecules with translational energy equal to or greater than that amount. In a simple theory of chemical kinetics, it is only those molecules that can surmount an “activation barrier” and react; this distribution therefore plays an important role in kinetics.

1.1.8 Hard-sphere collision rates

Let's begin thinking about molecules colliding with each other. Clearly that can be a complicated field; most of the richness of chemical reactions occurs in some sequence of bimolecular collisions, and if a single simple theory could describe everything about those collisions chemistry wouldn't be nearly so interesting. But, for starters, let's use a simple theory: think of molecules as little tiny marbles. The "hard-sphere" model can teach us a remarkable amount about molecular collisions.

I'll start out by thinking about one molecule as moving with speed v_{rel} through a forest of other, stationary, molecules. All the molecules are hard spheres with diameter d . As our one molecule moves along, if its trajectory takes its center within a distance d of the center of any other molecule, the two will hit. (See Figure 1.4.) In a time t , our molecule carves out a "collision cylinder" of volume $\pi d^2 v_{\text{rel}} t$; any other molecules whose centers are in that cylinder will collide with it. The number of such molecules is just the volume of the cylinder times the number density of the gas, $\mathcal{N} = N/V$. So the number of collisions one molecule makes per second, z , is

$$z = \pi d^2 v_{\text{rel}} \mathcal{N}. \quad (1.51)$$

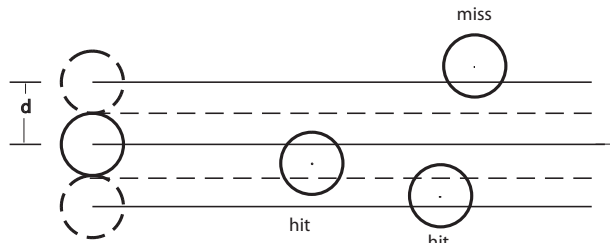


Figure 1.4: The collision cylinder. Your text will have a similar picture.

If we rewrite \mathcal{N} with the ideal gas law we find

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{PN_A}{RT} = \frac{P}{kT} \quad (1.52)$$

so that in terms of the pressure the collision rate of a single molecule is

$$z = \pi d^2 v_{\text{rel}} \frac{P}{kT} \quad (1.53)$$

The effective "target area" of the molecule, πd^2 , is often called the *collision cross section* and given the symbol σ . This idea of an effective size can be usefully

extended to many kinds of events other than hard-sphere collisions. Events that are less likely than simply bouncing—for example, chemical reaction—will have smaller cross sections.

Of course, all the molecules are moving, and not all with the same speed. When you include all the molecules' motions, the appropriate value for v_{rel} is just the average speed, but calculated with the *reduced* mass of the colliding pair:

$$v_{\text{rel}} = \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} \quad (1.54)$$

where, as usual, $\mu = m_1 m_2 / (m_1 + m_2)$ and m_1 and m_2 are the masses of the colliding molecules. (Once again, you can express μ in kg/mol and use R in the numerator rather than k .)

If two different kinds of molecules are colliding, they might have different sizes as well as different masses; in that case, you use the average diameter $d = (d_1 + d_2)/2$ in Eq. (1.53).

The formulas I have given so far describe the number of collisions a single molecule makes with other molecules (either the same kind or different) in a gas. In a gas that contains molecule types A and B, the number of A–B collisions per second per unit volume is

$$Z_{AB} = z_{AB} \mathcal{N}_A \quad (1.55)$$

$$Z_{AB} = \sigma_{AB} \left(\frac{8kT}{\pi\mu_{AB}} \right)^{\frac{1}{2}} \left(\frac{P_A}{kT} \right) \left(\frac{P_B}{kT} \right). \quad (1.56)$$

The number of B–B collisions per second per unit volume is calculated similarly, but we must divide by 2 to avoid counting the same collision twice:

$$Z_{BB} = \frac{1}{2} z_{BB} \mathcal{N}_B \quad (1.57)$$

$$Z_{BB} = \frac{1}{2} \sigma_{BB} \left(\frac{8kT}{\pi\mu_{BB}} \right)^{\frac{1}{2}} \left(\frac{P_B}{kT} \right)^2 \quad (1.58)$$

where $\mu_{BB} = m_B/2$, $\sigma_{BB} = \pi d_B^2$, and P_B is the partial pressure of B.

Mean free path

We have seen how to calculate the number of collisions a particular molecule makes with other molecules per second, and also how to calculate the average speed of the molecule. With those two results it is easy to find the average distance a molecule travels between collisions, the *mean free path* λ :

$$\lambda = \langle v \rangle / z = \frac{kT}{\sqrt{2}\sigma P}. \quad (1.59)$$

At one atmosphere and 300 K, for nitrogen and oxygen $\lambda \sim 160$ nm.

Chapter 2

Chemical Kinetics

2.1 Elementary reactions and rate laws

It is conventional to call the rate of change of concentration of a reactant or product the *rate* of a reaction. This definition is useful in homogeneous reaction mixtures at constant volume. (For other conditions, where unmixed flows, reactions at interfaces, or volume changes are important, different definitions of the reaction rate are needed.) The *rate law* is the differential equation that describes the rate as a function of concentrations of the chemical species present. If a chemical equation describes an *individual molecular event*, as for instance



then we say that equation represents an *elementary reaction*. (Most ordinary chemical equations are not elementary; they describe overall chemical processes that occur in several steps, not just one. One of the main goals of many kinetic studies is to determine the sequence of elementary reactions, or *mechanism*, which makes up an overall reaction.)

For an elementary bimolecular reaction, we would expect that the *rate* of the reaction should be proportional to the number of collisions between the reactants per second. In the gas phase we have already seen, in Eq. (1.56), that that collision rate Z_{AB} is proportional to the product of pressures of the two reactants. Equivalently, since $\frac{P}{RT} = \frac{n}{V}$, it is proportional to the concentrations of the two reactants. In solution, the reaction rate must similarly be proportional to the “encounter rate”, the number of times per second that the two reactants find one another. That rate in solution is also proportional to the product of the concentrations of the two species. For an elementary bimolecular reaction, then,

can write down the rate law directly:

$$-\frac{d[\text{O}]}{dt} = k[\text{O}][\text{CH}_4], \quad (2.2)$$

where k , the proportionality constant between the rate and the product of concentrations, is an *elementary rate coefficient*. The rate coefficient is usually a function of temperature but it does not depend on the concentrations, as you can see from Eq. (1.56).

Note that for an elementary reaction we can write the rate in terms of any of the concentrations, because

$$\text{rate} = -\frac{d[\text{O}]}{dt} = -\frac{d[\text{CH}_4]}{dt} = \frac{d[\text{OH}]}{dt} = \frac{d[\text{CH}_3]}{dt}. \quad (2.3)$$

I will sometimes follow a convention of using a double-tailed arrow, \rightleftharpoons , for reactions that are thought to be elementary. (Unlike the use of square brackets for concentrations, this convention is not a standard part of the kinetics nomenclature.)

Reaction (1) is a *bimolecular* reaction; the other possibilities are unimolecular and termolecular, both of which are rarer. Elementary unimolecular reactions come about when a reactant has been prepared somehow with enough energy to react on its own. For example, in a recent lab experiment, you prepared an electronically excited state of $\text{Ru}(\text{bpy})_3^{2+}$ by photoexcitation, which then fluoresced in an elementary unimolecular reaction:



The rate of such an elementary unimolecular reaction is simply proportional to the concentration of its single reactant, so its rate law is

$$\frac{d[\text{R}^*]}{dt} = -k_f[\text{R}^*]. \quad (2.5)$$

More commonly, unimolecular reactants are generated in bimolecular collisional processes that form part of an overall reaction mechanism.

2.2 Integrated rate laws

The rate law is a differential equation. The solution to that equation, the *integrated rate law*, describes the concentration of one species as a function of time. Let's examine three simple types of elementary rate laws: those for unimolecular

reactions, “simple” bimolecular reactions where the single reactant must collide with another molecule of the same species to react, and “mixed” bimolecular reactions where two different species must collide. In the general language of kinetics, these reactions give “first order”, “simple second order”, and “mixed second order” rate laws. Similar rate laws are also often found even for more complicated reactions composed of several steps, as we will see shortly.

2.2.1 First order reactions

While true first order reactions (even composite ones) are comparatively rare, first-order rate behavior is extremely important because many more complicated reactions can be “tricked” into behaving like first-order ones and first-order behavior is easier to handle experimentally than any other type.

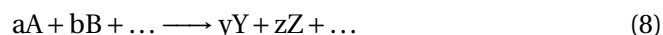
A first order unimolecular reaction



has the rate law

$$-\frac{d[A]}{dt} = k[A]. \quad (2.7)$$

If the general (not elementary) reaction



is first order with respect to A, and its rate depends on no other concentrations (it is zero order with respect to all other species), then its rate law is

$$-\frac{1}{a} \frac{d[A]}{dt} = k[A]. \quad (2.9)$$

The $\frac{1}{a}$ out front is a convention that makes the rate expressed in terms of any reactant or product equal if there are no intermediates with substantial concentrations. Notice that k must have units of s^{-1} ; that will always be true of first-order rate coefficients. k is a positive number that does not depend on any concentrations, though it does depend (usually strongly) on temperature.

Integration of the rate law

The rate law is a differential equation; in this case it is a *separable* equation, and can be solved simply by isolating the terms corresponding to the different

variables $[A]$ and t on different sides of the equation and integrating both sides:

$$\frac{d[A]}{[A]} = -k dt \quad (2.10)$$

$$\int \frac{1}{[A]} d[A] = -k \int dt \quad (2.11)$$

$$\ln[A] = -kt + C \quad (2.12)$$

C is an as-yet-unknown constant of integration. Exponentiating both sides we obtain

$$[A](t) = e^C e^{-kt} = C' e^{-kt}. \quad (2.13)$$

We must find the value of the constant C' by applying the initial conditions. At time $t = 0$, the concentration of A is A_0 . We therefore have $C' = A_0$, so that

$$[A](t) = A_0 e^{-kt} \quad (2.14)$$

and the concentration of A falls exponentially with time from its initial value.

The rate coefficient can be determined by measuring $[A]$ as a function of time. Figure 2.1 shows two common plots used to demonstrate or analyze this behavior.

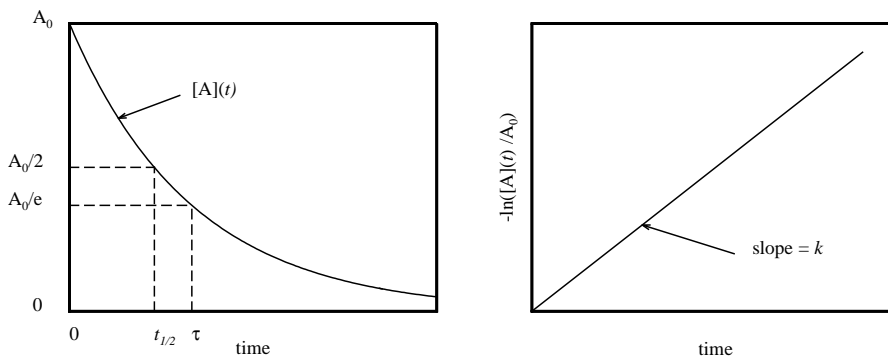


Figure 2.1: Concentration-vs.-time behavior for a simple first order reaction. The left panel shows the exponential concentration dependence; the right panel shows the linear behavior of a semilogarithmic plot.

Half-life and time constant

The *half-life* for a reaction is the time required for some reactant to reach half its initial concentration (or more precisely, for its concentration to reach a value halfway between its initial and final concentrations; for this case, the two definitions are the same.) For a first-order reaction we can find the half-life $t_{1/2}$ by substituting into Eq. (2.13):

$$[A](t_{1/2}) = \frac{A_0}{2} = A_0 e^{-kt_{1/2}} \quad (2.15)$$

$$\ln \frac{1}{2} = -k t_{1/2} \quad (2.16)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (2.17)$$

Notice that the half-life for a first order reaction is independent of the initial concentration of A; this is a very convenient property and is not true for other reaction orders.

The *time constant* τ of this reaction (also called the natural lifetime, the *e*-folding time, or the *1/e* time) is the time required for the concentration of A to reach $1/e$ (≈ 0.37) of its initial concentration. We can find it by a similar calculation:

$$[A](\tau) = \frac{A_0}{e} = A_0 e^{-k\tau} \quad (2.18)$$

$$\ln \frac{1}{e} = -k\tau \quad (2.19)$$

$$\tau = \frac{1}{k} \quad (2.20)$$

The *1/e* time is again independent of the initial concentration of A. Both the half-life $t_{1/2}$ and the *1/e* time τ have units of time: seconds, years, microseconds, or whatever. Both provide a quick-and-dirty way to estimate the first-order rate coefficient quickly from a plot of the concentration vs. time obtained in an experiment; just look to see how long it takes for the concentration to drop to half its initial value (to get $t_{1/2}$) or to just above $1/3$ of its initial value (to get τ). Then invert that time, and multiply by $\ln 2 \approx 0.7$ if you measured the half-life.

Analysis of first-order data

First-order reactions have an important property that makes them easier to study than others. If you can measure any property that is linearly related to the concentration (more precisely, *affine* in the concentration: $Q = \alpha[A] + \beta$), then you can determine the rate coefficient without having to know either α or β ; that is, the analytical method you use to measure $[A]$ need not be calibrated!

If A is a reactant, then you fit the Q vs. time data to an equation of the form

$$Q = Ce^{-kt} + D, \quad (2.21)$$

and if A is a product you fit to

$$Q = C(1 - e^{-kt}) + D, \quad (2.22)$$

and in either case the value of k is independent of the slope α and offset β in the expression $Q = \alpha[A] + \beta$.

Many textbooks will suggest that you use the equation

$$-\ln\left(\frac{Q - Q_\infty}{Q_0 - Q_\infty}\right) = kt \quad (2.23)$$

and therefore make a logarithmic plot to find k . However, this method has the disadvantages that (1) it relies too heavily on the precision of the single measurement Q_∞ at very long time, and (2) that it requires careful weighting of the data in the linear least-squares fit if an accurate value of k is required.

Examples of observables Q that are useful in analyzing first-order reactions include

1. mass of reaction mixture (for reactions evolving gases)
2. capillary rise
3. optical absorption
4. optical rotation in a polarimeter (classic)
5. fluorescence
6. mass spectrometer signal on either product or reactant mass

The crucial point is that you do not have to know how your “detector” is calibrated; you only have to know that its reading is proportional to the concentration (possibly with some offset).

2.2.2 Pseudo-first-order reactions

When a reaction is known to follow a rate law of higher order than 1, concentrations can often be adjusted to make the kinetics appear first order with an effective rate coefficient. Consider a reaction



with the rate law

$$-\frac{d[A]}{dt} = k[A][B]. \quad (2.25)$$

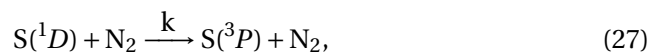
This rate law is second order overall, and its rate coefficient k has units $\text{M}^{-1} \text{s}^{-1}$. But if we run the reaction with a very large excess of B, say $B_0 = 100A_0$, then [B] will change very little during the reaction—it will be nearly equal to B_0 the whole time—and we can write

$$-\frac{d[A]}{dt} \approx k'[A], \quad (2.26)$$

where $k' = kB_0$. k' is a pseudo-first-order rate coefficient with units s^{-1} . Now, if we do this experiment at several different values of B_0 (all very large compared to A_0), extract a k' for each with an exponential fit as described above, and then plot k' vs. B_0 , we should get a straight line with slope k (that is, the true second-order rate coefficient). This is one of the best ways to measure second-order coefficients.

It's better to make that k' vs. B_0 plot and find its slope to get k than to evaluate k from the measured k' at a single B_0 . Using only a single measurement will get you the wrong answer if there is some competing process that can remove A from the system (such as a slow decomposition reaction).

Example As part of my graduate work I did an experiment that determined the rate coefficient for the reaction



which is a mixed second order reaction. In the experiment, I prepared a sample that contained a few millitorr of OCS, amounts of nitrogen ranging from 0.1 to 2 torr, and helium (which reacts extremely slowly with $S(^1D)$) to make the total pressure 5 torr. A fast pulse of laser light photolyzed the OCS to produce $S(^1D)$. I then detected the total amount of $S(^1D)$ by laser induced fluorescence as a function of time. Because the nitrogen concentration was much higher than that of the $S(^1D)$, the system was a good pseudo-first-order one. I fit the decay

Table 2.1 Pseudo-first-order rate coefficients for quenching of singlet sulfur by nitrogen.

N ₂ pressure/torr	0.1	0.5	2.0
$k_1/\mu\text{s}$	0.541	1.442	4.88

curves to exponential decays to determine pseudo-first-order rate coefficients k_1 , yielding the results shown in Table 2.1.

I then made a plot of those coefficients against the nitrogen pressure and fit a straight line, as shown in Figure 2.2. The slope of the fitted line gave a second-order rate coefficient of $2.3 \mu\text{s}^{-1} \text{ torr}^{-1}$, which at room temperature is equivalent to $7.1 \times 10^{-11} \text{ cm}^{-1} \text{ molec}^{-1} \text{ s}^{-1}$.

Note that the intercept in Figure 2.2 is not zero. Two processes, quenching by species other than nitrogen (namely OCS and helium) and diffusion of $\text{S}(^1D)$ out of the detection region, contribute to the pseudo-first-order rate coefficients. Making the plot against nitrogen pressure isolates the effect of the nitrogen from the competing processes and avoids the systematic errors they would otherwise introduce.

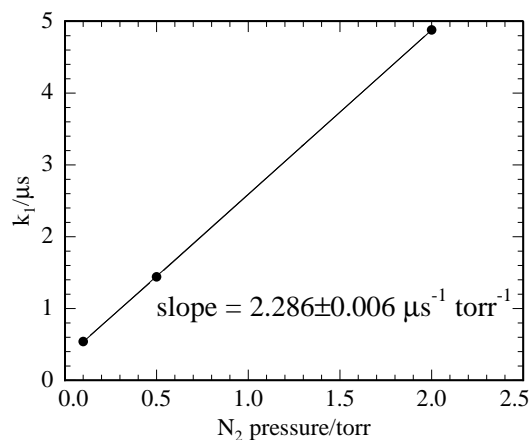


Figure 2.2: Extraction of second order rate coefficient from pseudo-first-order data in Table 2.1.

2.2.3 Reactions second order in a single reactant

Here we have

$$\frac{d[A]}{dt} = -k[A]^2 \quad (2.28)$$

$$\frac{d[A]}{[A]^2} = -k dt \quad (2.29)$$

$$\int \frac{d[A]}{[A]^2} = -k \int dt \quad (2.30)$$

$$-\frac{1}{[A]} = -kt + C \quad (2.31)$$

Applying the initial condition $[A](t=0) = A_0$ we find $C = -1/A_0$, so

$$\frac{1}{[A]} - \frac{1}{A_0} = kt \quad (2.32)$$

The textbook analysis is to plot $1/[A]$ against t and extract the slope to get k . Notice that the plot of $[A]$ vs. time is not exponential, as it is in the first-order case, but hyperbolic; the concentrations approach their asymptotic values much more slowly than in the first order reaction.

Look at the half-life now. By an analysis similar to that we used before, we find

$$t_{1/2} = \frac{1}{kA_0} \quad (2.33)$$

Now, the half-life depends on the initial concentration. In fact, it is inversely proportional to the initial concentration. If you double the initial reactant concentration, the half-life will be cut in half. Similarly, if you compare the first and second half-lives for a single reaction mixture, the second one is twice as long as the first (whereas in the first order case, they are the same.) This gives a quick and dirty way to estimate reaction orders from data.

2.2.4 Mixed second order reactions

One of the most common rate laws in practice is “mixed second order”: first order in each of two reactants. For the reaction



if A and B are consumed simultaneously we have

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = k[A][B]. \quad (2.35)$$

If A and B start with stoichiometric concentrations, $aB_0 = bA_0$, then this looks just like the previous case, since $a[A] = b[B]$ at all times.

Otherwise, we have two differential equations: one each in [A] and [B]. If A and B are consumed simultaneously (there are no intermediates of substantial concentrations) we can say

$$[B] = B_0 - \frac{b}{a} (A_0 - [A]), \quad (2.36)$$

so that

$$-\frac{1}{a} \frac{d[A]}{dt} = k[A] \left(B_0 - \frac{b}{a} (A_0 - [A]) \right) \quad (2.37)$$

$$-\frac{d[A]}{dt} = k[A] (aB_0 - bA_0 + b[A]) \quad (2.38)$$

$$= k[A] (\Delta_0 + b[A]) \quad (2.39)$$

where $\Delta_0 = aB_0 - bA_0$. This differential equation is separable. Separating it, using the standard indefinite integral

$$\int \frac{dx}{x(a+bx)} = \frac{-1}{a} \ln \frac{a+bx}{x} + C, \quad (2.40)$$

applying the initial condition, and substituting back in for [B] gives

$$\ln \left(\frac{[B]}{[A]} \right) = \ln \left(\frac{B_0}{A_0} \right) + k\Delta_0 t. \quad (2.41)$$

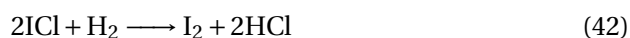
So, a plot of $\ln([B]/[A])$ against t gives a straight line with slope $k\Delta_0$.

As A_0 and B_0 become closer to stoichiometric concentrations, Δ_0 becomes closer to zero, and the relative uncertainty in its value (from errors in the initial concentrations A_0 and B_0) becomes larger. This method is numerically unsuitable near stoichiometric initial concentrations. It's usually best to run kinetic experiments under conditions where one reactant is clearly the limiting reactant, or else to use stoichiometric initial concentrations and use the simple second order analysis.

2.3 Mechanisms

The *mechanism* lists the elementary reactions making up a chemical process. It can be used to predict the detailed concentration vs. time behavior and therefore the observed rate law. A proposed mechanism cannot be proven correct, though it can be proven wrong by disagreement with observed behavior. Adding together the reactions of the mechanism (perhaps with multipliers, indicating that some elementary steps must happen more than once) should give the overall reaction.

For example, the “laboratory” reaction



has the observed rate law

$$\frac{1}{2} \frac{d[\text{HCl}]}{dt} = k[\text{ICl}][\text{H}_2]. \quad (2.43)$$

This rate law *suggests* that the kinetics are dominated by a bimolecular reaction between ICl and H₂. One possibility for the mechanism is



We will shortly see how to analyze the behavior of this mechanism quantitatively.

2.3.1 Simple example: reversible unimolecular transformation

The mechanism



which can also be written



gives the set of “elementary rate laws”

$$\frac{d[\text{A}]}{dt} = -k_1[\text{A}] + k_2[\text{B}] \quad (2.49)$$

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}] - k_2[\text{B}] \quad (2.50)$$

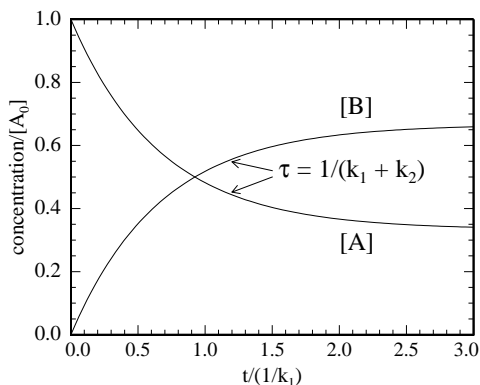


Figure 2.3: Behavior of a reversible first order reaction for the case $B_0 = 0$ and $k_1 = 2k_2$.

This is a system of two coupled ODEs. Once the initial conditions are specified, its solution describes the complete time dependence. Figure 2.3 shows a graphical representation of the concentration vs. time profiles of both components when $B_0 = 0$. In this case, the system of equations can be easily solved analytically, and I will now show how to do that. In more complicated cases I will leave out the detailed solutions.

We can solve the system by using mass balance to uncouple the two equations: $[B] = B_0 + (A_0 - [A])$ from stoichiometry, so that

$$\frac{d[A]}{dt} = -k_1[A] + k_2(B_0 + A_0 - [A]). \quad (2.51)$$

Eq. (2.51) is now a separable differential equation in $[A]$ only. Its solution, with $[A](t=0) = A_0$, is

$$[A](t) = \frac{1}{k_1 + k_2} \left\{ (k_1 A_0 - k_2 B_0) e^{-(k_1 + k_2)t} + k_2 (A_0 + B_0) \right\} \quad (2.52)$$

The rate law in this case looks like

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] - k_2(B_0 + A_0) \quad (2.53)$$

$$= k'[A] + C, \quad (2.54)$$

and the reaction order is not defined.

At equilibrium, the forward and reverse rates are the same, so

$$k_1[A]_{\text{eq}} = k_2[B]_{\text{eq}} \quad (2.55)$$

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_2} \quad (2.56)$$

$$= K_{\text{eq}} \quad (2.57)$$

Many exact solutions of this type are given by Z. G. Szabó, in *Comprehensive Chemical Kinetics*, vol. 2, ch. 1, ed. by Bamford and Tipper (Elsevier, Amsterdam, 1969.)

2.4 Exact and approximate analytic solutions to sets of rate equations

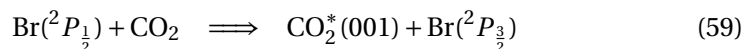
Any kinetic system composed entirely of first-order (or pseudo-first-order!) steps has an exact analytic solution. It may be found by the linear algebraic methods described in Sec. 2.5 in Steinfeld, Francisco, and Hase. Moderately complicated systems can also be handled with Laplace transforms, described in Sec. 2.4 of the same text. These techniques work only for linear (1st-order) systems. Let's consider qualitatively a few simple cases, where the higher-powered solution techniques are unnecessary.

2.4.1 Consecutive first-order reactions

Consider the *consecutive* mechanism



An example of this sort of system is the electronic quenching of excited bromine atoms by CO₂,



under conditions of excess CO₂ so that it is pseudo first order. One way to monitor the reaction progress is to measure IR luminescence of Br(^2P_{1/2}) or CO₂*.

The differential equation describing [A] is the usual one corresponding to first-order decay, so that A decays exponentially with $\tau = 1/k_1$. If you substitute the exponential decay into the equation for $d[B]/dt$, you get a "first order linear"

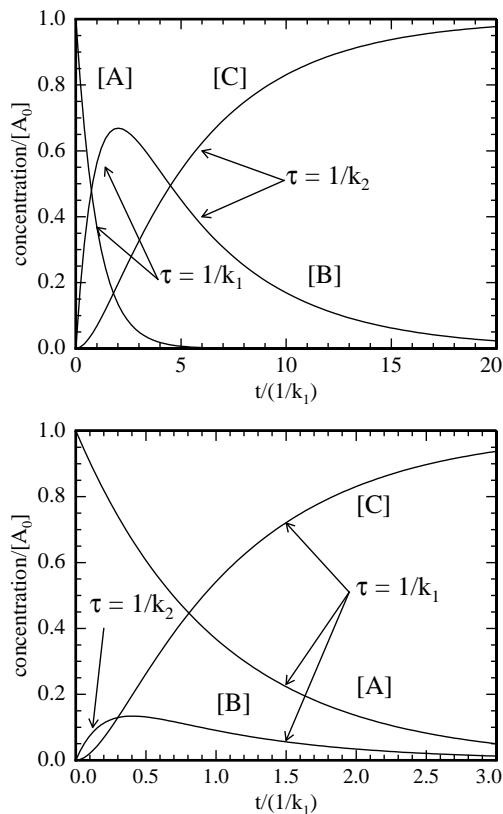


Figure 2.4: Temporal behavior of consecutive, irreversible first-order reactions. The upper panel shows the case $k_1 = 5k_2$; the lower panel shows the case $k_2 = 5k_1$.

(not separable) differential equation. It can be solved by techniques described in every differential equations textbook. [B] grows, then decays:

$$[B] = \frac{k_1 A_0}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) \quad (2.61)$$

The maximum concentration of B depends on the relative sizes of k_1 and k_2 . Let's look at the two extreme cases, illustrated in the upper and lower panels of Figure 2.4.

Consecutive 1st-order, $k_1 \gg k_2$

In this case, then at short times ($t \sim 0$), the second exponential term in Eq. (2.61) is near 1, the equation looks like $B \approx A_0(1 - e^{-k_1 t})$, and B grows in with time constant $1/k_1$ as though no conversion to C was occurring. At long times, the first of the two exponential terms goes toward zero, and we have $[B] \approx A_0 e^{-k_2 t}$, so that B is decaying toward C with time constant $1/k_2$. The system essentially converts all the A to B, and then, on a slower timescale, converts the B to C. The maximum concentration of B will be nearly the initial concentration of A.

We can get [C] by mass balance: $[C] = A_0 - [A] - [B]$.

Consecutive 1st-order, $k_1 \ll k_2$

In this case, a B molecule decays to C almost as soon as it is formed; only very small concentrations of B ever appear. Once a small “steady-state” concentration of B has built up, it looks like C is appearing with the same rate that A is disappearing, so C appears with roughly an exponential rise that has $\tau \sim 1/k_1$. We will see that this simple system, with its short-lived intermediate B, is an example of systems for which the *steady state approximation* is useful.

2.4.2 Competitive (parallel) first order reactions

In this case, the mechanism is



The rate equations are

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] \quad (2.64)$$

$$\frac{d[B]}{dt} = k_1[A] \quad (2.65)$$

$$\frac{d[C]}{dt} = k_2[A] \quad (2.66)$$

The first of the three is an ordinary first-order decay, giving $[A] = A_0 e^{-(k_1+k_2)t}$. Substituting that result into the second and third equations gives separable equa-

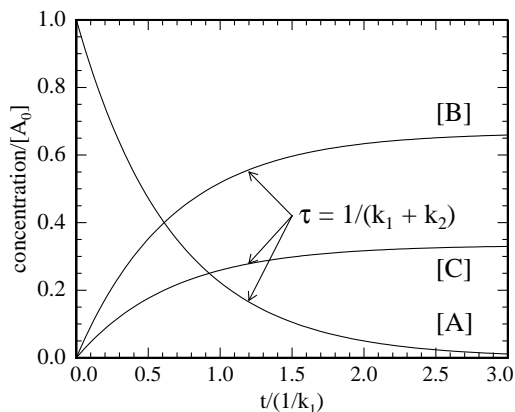


Figure 2.5: Temporal behavior of competing, irreversible first-order reactions. In this figure $k_1 = 2k_2$.

tions for both B and C, which have nearly the same solutions:

$$[B] = \frac{k_1 A_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t}) \quad (2.67)$$

$$[C] = \frac{k_2 A_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t}) \quad (2.68)$$

Note that B and C have the same temporal behavior; their risetimes are determined by the sum of the two elementary rate coefficients. Their concentrations are determined by the individual rate constants, such that $[B]/[C] = k_1/k_2$ always. Such systems are convenient to study experimentally; measure τ_A to get $k_1 + k_2$, then simply measure $\frac{[B]}{[C]}$ at any convenient time (typically $t \rightarrow \infty$) to get the ratio k_1/k_2 . Those two measurements are enough to determine the individual k values. This approach is the basis of the very popular “relative rates method” of experimental kinetics.

Kinetic vs. thermodynamic control

If the reactions are reversible,



then the issue of thermodynamic or kinetic control of products appears.

Assuming no direct interconversion of B and C,

$$\frac{[B]_{\text{eq}}}{[C]_{\text{eq}}} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} \cdot \frac{[A]_{\text{eq}}}{[C]_{\text{eq}}} = \frac{k_1}{k_{-1}} \frac{k_{-2}}{k_2} = K_{\text{BC}}. \quad (2.71)$$

If $k_1 k_{-2} \ll k_{-1} k_2$ so that $K_{\text{BC}} \ll 1$, then at equilibrium there will be much more C than B and we say that C is the “thermodynamically favored” product. On the other hand, if $k_1 \gg k_{-1}$ and $k_2 \gg k_{-2}$, both elementary reactions will “act irreversible”—their forward rates will be much greater than their reverse ones—until most of the A is gone. During that time the ratio $[B]/[C] \approx k_1/k_2$. If $k_1 \gg k_2$, mostly B will appear. B is then called the “kinetically favored” product. These conditions on the rate coefficients are not mutually exclusive, and the effect is not at all rare. If

$$\begin{aligned} k_1 &= 10^0 \text{ s}^{-1} & k_{-1} &= 10^{-7} \\ k_2 &= 10^{-2} & k_{-2} &= 10^{-12} \end{aligned}$$

then Table 2.2 shows the resulting concentrations. This is a not-too-extreme case of kinetic control.

Table 2.2 Kinetic control

time	[A](%)	[B](%)	[C](%)
0	100	0	0
10 s	0	99	1
3 months	0	98	2
1900 years	0	1	99

Relative Rate Experiments

Consider elementary reaction of B with two compounds A_1 and A_2 , to give products P_1 and P_2 .



If B is added to a *mixture* of A₁ and A₂, whose concentrations are $\gg B_0$, then

$$\frac{d[P_1]}{dt} = k_1[A_1]_0[B] \quad (2.74)$$

$$\frac{d[P_2]}{dt} = k_2[A_2]_0[B] \quad (2.75)$$

$$\frac{d[P_1]}{d[P_2]} = \frac{k_1[A_1]_0}{k_2[A_2]_0} \quad (2.76)$$

So, after a long time

$$\frac{[P_1]_\infty}{[P_2]_\infty} = \frac{k_1[A_1]_0}{k_2[A_2]_0} \quad (2.77)$$

If either k_1 or k_2 is known from other measurements, this technique allows determination of the other *without* a concentration-vs.-time experiment; just let B react to completion with a mixture of A₁ and A₂, then analyze the products when the reaction is over. This *relative rate* technique has been used extensively to measure reaction rates of radicals.

Example: Generate phenyl radicals (C₆H₅·) by pyrolysis of a precursor, in the presence of both a hydrocarbon RH and CCl₄. After the reaction, measure the ratio [C₆H₅Cl]/[C₆H₆]. That ratio times $\frac{[RH]_0}{[CCl_4]_0}$ gives the ratio of rate constants k_{CCl_4}/k_{RH} . Careful work requires several starting ratios; then from Eq. (2.77) plotting the final product ratio vs. the initial reactant ratio yields k_1/k_2 as the slope, and a zero intercept.

The advantage of relative rate techniques is that slow but quantitative analytical techniques (gas chromatography, wet-chemical analysis, etc) can be used to study even fast reactions.

2.5 Approximations

What to do if a mechanism is too complicated to usefully compare its predictions with data?

In particular, mechanisms give concentration vs. time for all species. Usually we can obtain the rate law only in terms of the reactants or products or both. So we seek a method to eliminate the concentrations of intermediates in our rate expressions.

A common kind of mechanism involving an intermediate follows the pattern



The net reaction is $A + C \longrightarrow D$; B is an intermediate. The set of elementary rate laws is

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] \quad (2.80)$$

$$\frac{d[B]}{dt} = k_1[A] - (k_{-1} + k_2[C])[B] \quad (2.81)$$

$$\frac{d[C]}{dt} = -k_2[B][C] \quad (2.82)$$

$$\frac{d[D]}{dt} = k_2[B][C] \quad (2.83)$$

Steady-state approximation

If B is a very reactive species (perhaps an organic free radical), we might assume that its concentration remains small throughout the reaction. Then the absolute *slope* of its concentration will be small compared to other time dependences in the system, and we write

$$\frac{d[B]}{dt} \approx 0. \quad (2.84)$$

We then use that assumption to eliminate [B] from the rate expressions for the product D. This is called the steady-state or Bodenstein approximation. For our example mechanism we have

$$\frac{d[B]}{dt} \stackrel{\text{SSA}}{\approx} 0 = k_1[A] - (k_{-1} + k_2[C])[B] \quad (2.85)$$

$$[B] \stackrel{\text{SSA}}{\approx} \frac{k_1[A]}{k_{-1} + k_2[C]} \quad (2.86)$$

$$\frac{d[D]}{dt} \stackrel{\text{SSA}}{\approx} \frac{k_1 k_2 [A][C]}{k_{-1} + k_2[C]} \quad (2.87)$$

Now if $k_{-1} \gg k_2[C]$,

$$\frac{d[D]}{dt} \stackrel{\text{SSA}}{\approx} \frac{k_1 k_2}{k_{-1}} [A][C] \quad (\text{apparent 2nd order,}) \quad (2.88)$$

while if $k_2[C] \gg k_{-1}$,

$$\frac{d[D]}{dt} \stackrel{\text{SSA}}{\approx} k_1 [A] \quad (\text{apparent 1st order.}) \quad (2.89)$$

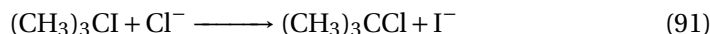
Conditions for validity of SSA It is sufficient that the sum of all effective rate coefficients “out of” the intermediate be much greater than the sum “into” the intermediate. In our example, this means

$$(k_{-1} + k_2[\text{C}]) \gg k_1. \quad (2.90)$$

(It’s generally safe to take “ \gg ” to mean “greater by a factor of 50 or more”; smaller ratios are often acceptable.)

In addition, there must be a “build-up time” during which [B] climbs to its (small) steady-state value, and $\frac{d[\text{B}]}{dt} \approx 0$ must be incorrect. The characteristic time for buildup of the intermediate concentration is the inverse of the total effective rate coefficient for loss of B, $(k_{-1} + k_2[\text{C}])^{-1}$, and after a few times that characteristic time the steady state is established.

Example The classic example of an $\text{S}_{\text{N}}1$ reaction from organic chemistry is the nucleophilic substitution of a tertiary halide:

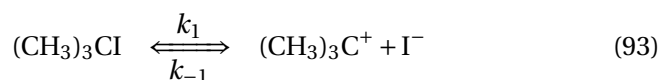


whose observed rate law is under most conditions is first order in *t*-butyl iodide but independent of the chloride concentration:

$$\frac{d[\text{TBCl}]}{dt} = k[\text{TBI}], \quad (2.92)$$

where I have written TBCl for *t*-butyl chloride and TBI for *t*-butyl iodide.

A likely mechanism is



Writing TB^+ for the carbocation intermediate, the rate of production of product is

$$\frac{d[\text{TBCl}]}{dt} = k_2[\text{TB}^+][\text{Cl}^-]. \quad (2.95)$$

This elementary rate law contains the concentration of the intermediate TB^+ ; for comparison to the observed rate law we need to eliminate it from the expression.

Applying the steady-state approximation to TB^+ , we find

$$\frac{d[\text{TB}^+]}{dt} = k_1[\text{TBI}] - k_{-1}[\text{TB}^+][\text{I}^-] - k_2[\text{TB}^+][\text{Cl}^-] \stackrel{\text{SSA}}{\approx} 0 \quad (2.96)$$

$$[\text{TB}^+] \stackrel{\text{SSA}}{\approx} \frac{k_1[\text{TBI}]}{k_{-1}[\text{I}^-] + k_2[\text{Cl}^-]}. \quad (2.97)$$

Inserting that result into the product production rate expression gives

$$\frac{d[\text{TBCl}]}{dt} \stackrel{\text{SSA}}{\approx} k_2[\text{Cl}^-] \frac{k_1[\text{TBI}]}{k_{-1}[\text{I}^-] + k_2[\text{Cl}^-]}. \quad (2.98)$$

Now, if the rate coefficients and concentrations are such that $k_2[\text{Cl}^-] \gg k_{-1}[\text{I}^-]$, then $k_{-1}[\text{I}^-]$ is negligible in the denominator, the $k_2[\text{Cl}^-]$ terms cancel top and bottom, and the predicted rate law is

$$\frac{d[\text{TBCl}]}{dt} \approx k_1[\text{TBI}] \quad (2.99)$$

in agreement with the observed rate law. The observed rate coefficient k in this case is simply k_1 .

2.5.1 Other Simplifying Approximations

Once again, consider the mechanism



and let us look for an expression for $\frac{d[\text{C}]}{dt}$. We have the set of rate equations

$$\frac{d[\text{A}]}{dt} = -k_1[\text{A}] + k_{-1}[\text{B}] \quad (2.102)$$

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}] - (k_{-1} + k_2)[\text{B}] \quad (2.103)$$

$$\frac{d[\text{C}]}{dt} = k_2[\text{B}] \quad (2.104)$$

I want to consider two main cases, illustrated in Figure 2.6 and summarized in Table 2.3.

Table 2.3 Relations among simplifying approximations.

Case	Requirements	Long-time rate coefficient
SSA	$(k_{-1} + k_2) \gg k_1$	$k_1 k_2 / (k_{-1} + k_2)$
REA	$(k_1 + k_{-1}) \gg k_2$	$k_1 k_2 / (k_1 + k_{-1})$
SS-EQ	$k_{-1} \gg k_1$ and $k_{-1} \gg k_2$	$k_1 k_2 / k_{-1}$

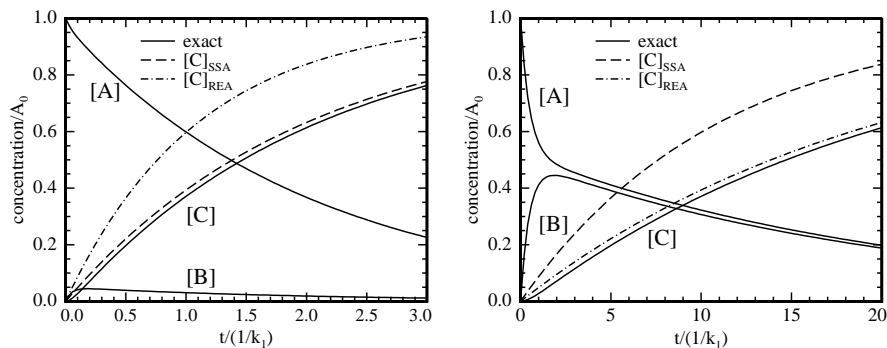


Figure 2.6: The steady-state and equilibrium approximations for the $A \rightleftharpoons B \rightarrow C$ mechanism, for two different sets of rate coefficients. In the left panel $k_{-1} = k_2 = 10k_1$; in the right panel $k_1 = k_{-1} = 10k_2$.

Rapid equilibrium case: $(k_1 + k_{-1}) \gg k_2$

The rate equations for A and B now look like the simple system $A \rightleftharpoons B$, whose solution was worked out in Section 2.3.1. After a time $\approx 1/(k_1 + k_{-1})$, the $A \rightleftharpoons B$ reaction will reach approximate equilibrium so that $[B] \approx \frac{k_1}{k_{-1}}[A]$. A and B will act like a single species that is slowly decaying toward C, and

$$\frac{d[C]}{dt} \text{ REA} \approx \frac{k_1 k_2}{k_{-1}} [A] \quad (2.105)$$

This is the “rapid equilibrium approximation.”

Steady state case: $(k_{-1} + k_2) \gg k_1$

This is just the requirement for the steady-state approximation. Applying it to this case gives

$$\frac{d[B]}{dt} = -k_1[A] - (k_{-1} + k_2)[B] \stackrel{\text{SSA}}{\approx} 0 \quad (2.106)$$

so

$$[B] \stackrel{\text{SSA}}{\approx} \frac{k_1 [A]}{(k_{-1} + k_2)} \quad (2.107)$$

$$\frac{d[C]}{dt} \stackrel{\text{SSA}}{\approx} \left(\frac{k_1 k_2}{k_{-1} + k_2} \right) [A] \quad (2.108)$$

Equilibrium-steady-state case

If, in the steady-state case, $k_{-1} \gg k_2$, or, in the rapid equilibrium case, $k_{-1} \gg k_1$, then these two approximations reduce to a common result, which Pyun (*J. Chem. Ed.* **48**, 194 (1971)) calls the “equilibrium-steady-state solution”. This simplest approximation requires that k_{-1} be the fastest rate coefficient in the system.

After the time required for the establishment of either the steady state or the rapid equilibrium condition, C begins appearing (in this first-order example) with a simple exponential behavior. The effective rate coefficient for this appearance is given in Table 2.3.

2.5.2 Rate determining steps

In some cases, the overall reaction rate is dominated by one of the elementary steps, and that step is called the “rate-determining” or “rate-controlling” step.

In the steady-state approximation, if $k_2 \gg k_{-1}$, then the long-time rate coefficient reduces simply to k_1 . In that case the formation of B from A is limiting the overall rate, and we say that the first step is rate-determining.

In the rapid equilibrium approximation, if $k_1 \gg k_{-1}$, then the A—B equilibrium lies heavily in the direction of B, and the long-time rate coefficient becomes simply k_2 . In this case the second step is the rate controlling one.

If the combined SSA-EQ approximation holds, then C appears with an effective rate coefficient that is the product of the rate coefficient for the second step and the equilibrium constant for the first step. In this case, the second step is again the rate controlling one, but the apparent rate coefficient (if one tries to model the mechanism with a simple $A \rightarrow C$ elementary step) is modified by the equilibrium constant for the initial equilibrium.

Notice that a single rate-controlling step does not always exist. For example, in a sequence of consecutive first-order transformations, if all the steps have the same rate coefficient then no one of them dominates the rate. (In other words, if you changed any one of them slightly, the overall rate of production of product would change.)

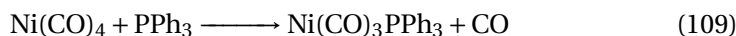
These various approximations - SSA, rapid equilibrium, rate-controlling step, etc. - are often more valuable for the chemical insight they provide than for mathematical power. In many cases they can be used to focus attention on the particular parts of a mechanism that are most important in determining the rate.

Whenever one or more assumptions about the values of rate coefficients are made, it is worthwhile to check the range of validity of the assumptions with numerical work.

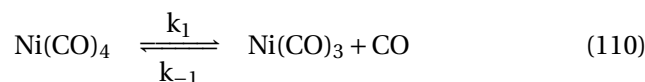
2.5.3 Examples

Ligand substitution

The nucleophilic substitution reaction



has the proposed mechanism (J. P. Day et al., JACS (90), 6927 (1968))



Applying the steady-state approximation to the unsaturated intermediate $\text{Ni}(\text{CO})_3$ gives

$$\frac{d}{dt}[\text{Ni}(\text{CO})_3] = k_1[\text{Ni}(\text{CO})_4] - (k_{-1}[\text{CO}] + k_2[\text{PPh}_3])[\text{Ni}(\text{CO})_3] \quad (2.112)$$

$$[\text{Ni}(\text{CO})_3] \stackrel{\text{SSA}}{\approx} \frac{k_1[\text{Ni}(\text{CO})_4]}{k_{-1}[\text{CO}] + k_2[\text{PPh}_3]} \quad (2.113)$$

$$\frac{d}{dt}[\text{Ni}(\text{CO})_3\text{PPh}_3] = k_2[\text{Ni}(\text{CO})_3][\text{PPh}_3] \quad (2.114)$$

$$\stackrel{\text{SSA}}{\approx} k_2[\text{PPh}_3] \frac{k_1[\text{Ni}(\text{CO})_4]}{k_{-1}[\text{CO}] + k_2[\text{PPh}_3]} \quad (2.115)$$

Under conditions of high ligand (PPh_3) concentration, the rate law will reduce to

$$\frac{d}{dt}[\text{Ni}(\text{CO})_3\text{PPh}_3] \approx k_1[\text{Ni}(\text{CO})_4], \quad (2.116)$$

that is, first order in the carbonyl concentration only. This is a common kinetic behavior seen for metal carbonyl nucleophilic substitutions.

Dinitrogen pentoxide decomposition

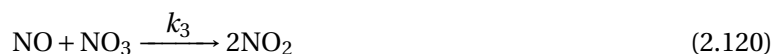
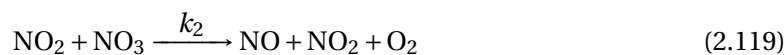
The reaction



follows an observed first-order rate law. The reaction between N_2O_5 and NO also looks first order but is much faster. NO_3 , a blue gas, also appears as an intermediate. A page from Johnston showing some data is reproduced in Figure 2.7.

Figure 2.7: Data on dinitrogen pentoxide decomposition (from Johnston, *Gas Phase Reaction Rate Theory*).

First-order kinetics suggests a unimolecular reaction as an important step.
Try this:



We shall try to find an expression for $\frac{d[\text{NO}_2]}{dt}$.

$$\frac{d[\text{NO}_2]}{dt} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] + 2k_3[\text{NO}][\text{NO}_3] \quad (2.121)$$

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - (k_{-1} + k_2)[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{NO}_3] \quad (2.122)$$

Apply SSA to NO_3 :

$$\frac{d[\text{NO}_3]}{dt} \stackrel{\text{SSA}}{\approx} 0 \quad (2.123)$$

$$[\text{NO}_3] \stackrel{\text{SSA}}{\approx} \frac{k_1[\text{N}_2\text{O}_5]}{(k_{-1} + k_2)[\text{NO}_2] + k_3[\text{NO}]} \quad (2.124)$$

Substitute into $\frac{d[\text{NO}_2]}{dt}$ expression:

$$\frac{d[\text{NO}_2]}{dt} \stackrel{\text{SSA}}{\approx} k_1[\text{N}_2\text{O}_5] \left\{ 1 - \frac{k_1[\text{NO}_2] + -2k_3[\text{NO}]}{(k_{-1} + k_2)[\text{NO}_2] + k_3[\text{NO}]} \right\} \quad (2.125)$$

$$\frac{d[\text{NO}_2]}{dt} \stackrel{\text{SSA}}{\approx} k_1[\text{N}_2\text{O}_5] \left\{ \frac{k_2[\text{NO}_2] + 3k_3[\text{NO}]}{(k_{-1} + k_2)[\text{NO}_2] + k_3[\text{NO}]} \right\} \quad (2.126)$$

This is still pretty ugly. Since NO is consumed quickly on the timescale of this reaction, try applying SSA to NO as well.

$$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{NO}_3] \stackrel{\text{SSA}}{\approx} 0 \quad (2.127)$$

$$[\text{NO}] \stackrel{\text{SSA}}{\approx} \frac{k_2}{k_3}[\text{NO}_2] \quad (2.128)$$

so

$$\frac{d[\text{NO}_2]}{dt} \stackrel{\text{SSA}}{\approx} k_1[\text{N}_2\text{O}_5] \left\{ \frac{k_2[\text{NO}_2] + 3k_2[\text{NO}_2]}{(k_{-1} + 2k_2)[\text{NO}_2]} \right\} \quad (2.129)$$

$$\frac{d[\text{NO}_2]}{dt} \stackrel{\text{SSA}}{\approx} \frac{4k_1k_2}{k_{-1} + 2k_2}[\text{N}_2\text{O}_5] \quad (2.130)$$

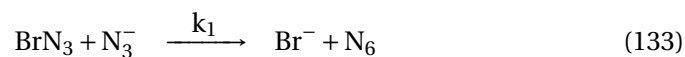
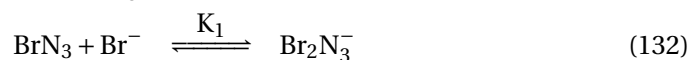
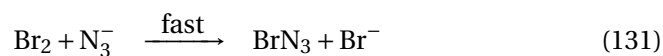
So with these two approximations we have found a first-order rate law, as observed.

The most common approach in steady-state treatments is to eliminate the concentrations of presumed intermediates, in order to find a rate law in terms of reactant or product concentrations only. The formation of “effective” or “observed” rate coefficients in terms of elementary ones usually becomes clear, but it is not always obvious that the SSA should hold at all.

Oxidation of aqueous azide

This example shows both the use of the steady-state treatment for an unstable intermediate and the effect of rapid equilibria that precede a rate-determining step.

A simplified mechanism for the oxidation of azide ion by aqueous Br_2 is



The reaction was followed under conditions of excess N_3^- and Br^- by observing the appearance of N_2 gas (T. S. Vivekanadam et al., *Int. J. Chem. Kin.* **13**, 199 (1981).) The product appeared with an apparent first-order behavior that depended linearly on $[\text{N}_3^-]$. The intermediate N_6 is an obvious candidate for the steady state approximation:

$$[\text{N}_6] \stackrel{\text{SSA}}{\approx} \frac{k_1}{k_3} [\text{BrN}_3][\text{N}_3^-] \quad (2.135)$$

$$\frac{d[\text{N}_2]}{dt} = 3k_3[\text{N}_6] \quad (2.136)$$

$$\stackrel{\text{SSA}}{\approx} 3k_1[\text{BrN}_3][\text{N}_3^-] \quad (2.137)$$

The first reaction is “fast”, so it is reasonable to regard the initially added bromine as converted completely to BrN_3 immediately. The BrN_3 can either be complexed by Br^- in step 132, or react to form product in step 133. The equilibrium gives us

$$[\text{Br}_2\text{N}_3^-] \stackrel{\text{REA}}{\approx} K_1 [\text{BrN}_3][\text{Br}^-] \quad (2.138)$$

When rapid equilibria are present, it is often useful to define a quantity whose value does not change so long as no reactions other than the equilibrium reactions occur. In this case we can define a quantity that is the total concentration of oxidized bromine, and examine its kinetics.

$$M = [\text{BrN}_3] + [\text{Br}_2\text{N}_3^-] \quad (2.139)$$

$$\stackrel{\text{REA}}{\approx} [\text{BrN}_3] + K_1 [\text{BrN}_3] [\text{Br}^-] \quad (2.140)$$

$$\stackrel{\text{REA}}{\approx} [\text{BrN}_3] (1 + K_1 [\text{Br}^-]) \quad (2.141)$$

$$[\text{BrN}_3] \stackrel{\text{REA}}{\approx} \frac{M}{1 + K_1 [\text{Br}^-]} \quad (2.142)$$

Since M is only destroyed in step Eq. (133),

$$\frac{dM}{dt} = -k_1 [\text{BrN}_3] [\text{N}_3^-] \quad (2.143)$$

$$\stackrel{\text{REA}}{\approx} -k_1 [\text{N}_3^-] \frac{M}{1 + K_1 [\text{Br}^-]} \quad (2.144)$$

Note that $\frac{dM}{dt}$ is just proportional to the rate of appearance of product, and that it should be expected to follow pseudo-first-order kinetics under conditions of constant $[\text{N}_3^-]$ and $[\text{Br}]$. The effective first-order rate coefficient is

$$k_{\text{eff}} = [\text{N}_3^-] \frac{k_1}{1 + K_1 [\text{Br}^-]}. \quad (2.145)$$

The appearance of several terms in the denominator of a rate expression is a common effect of equilibria that precede a rate-determining step.

Notice that bromide acts to inhibit the reaction by tying up the oxidized bromine (the oxidizing agent) in the unreactive complex Br_2N_3^- . The standard experimental analysis of this sort of competitive equilibrium is to measure k_{eff} at several values of $[\text{Br}^-]$, and make a plot of $[\text{N}_3^-]/k_{\text{eff}}$ against $[\text{Br}^-]$. The intercept of such a plot is $1/k_1$, and its slope is K_1/k_1 .

In fact, the complex can add another bromide ion to form $\text{Br}_3\text{N}_3^{2-}$, and the Br_2N_3^- can react with azide to produce N_6 with a smaller rate coefficient than k_1 . This additional component to the equilibrium and additional pathway to products do not change the basic pseudo-first-order nature of the reaction, but they make the expression for k_{eff} more complicated.

2.6 Construction of candidate mechanisms from rate laws

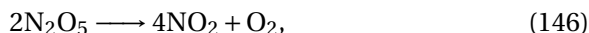
2.6.1 Mechanism construction rules

A carefully determined rate law can be interpreted to obtain the atomic composition and charge of the important transition states (highest point in each section of the free-energy diagram), and often some information about reactions prior to the RCS. It never (without studies specifically on the elementary reactions making up the mechanism) tells about fast reactions that follow the RCS.

Espenson gives a set of guidelines for interpretation of rate laws which I'll describe. These depend on accuracy of the steady-state and equilibrium approximations in appropriate parts of the mechanism, and usually on the existence of a single rate-controlling step at a given set of reactant concentrations. They are not foolproof but are sensible and useful. A similar set is given in Levine's book.

1. If the rate law is written in terms of the predominant species in the reaction medium, the composition and charge of the transition state for the RCS is the "algebraic value" of the concentration terms in the observed rate law. An undetermined number of solvent molecules may also be present in the transition state.

In our example from section 7.6,

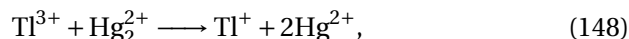


with rate law

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5], \quad (2.147)$$

the transition state for the slow step simply has the composition N_2O_5 .

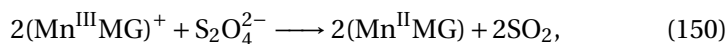
In the aqueous redox reaction



$$\text{rate} = k \frac{[\text{Tl}^{3+}][\text{Hg}_2^{2+}]}{[\text{Hg}^{2+}]}. \quad (2.149)$$

We "divide out" the denominator, to obtain a transition state composition of TlHg , and a transition state charge of $3+$.

For orders of $\frac{1}{2}$, use only half the atoms:

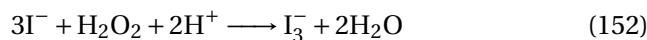


where MG is the protein myoglobin, has the rate law

$$\text{rate} = k[(\text{Mn}^{\text{III}}\text{MG})^+][\text{S}_2\text{O}_4^{2-}]^{\frac{1}{2}}, \quad (2.151)$$

and the TS is thought to have the composition Mn MG SO₂ with no charge.

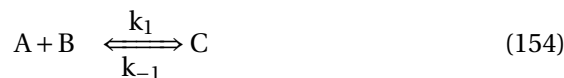
2. A sum of positive terms in the rate indicates independent parallel pathways to the same product. The composition and charge of the transition state along each pathway is found as above.



$$\frac{d[\text{I}_3^-]}{dt} = k_a[\text{I}^-][\text{H}_2\text{O}_2] + k_b[\text{I}^-][\text{H}_2\text{O}_2][\text{H}^+] \quad (2.153)$$

This acid-catalyzed reaction would be studied by monitoring the formation of I₃⁻ in various pH buffered solutions. k_a could be determined by extrapolation to zero [H⁺]. There are two pathways, plain and catalyzed, with compositions in the TS of (H₂O₂I)⁻ and H₃O₂I.

We can see how this example comes about in a simple case:



Applying SSA to C,

$$0 \stackrel{\text{SSA}}{\approx} \frac{d[\text{C}]}{dt} = k_1[\text{A}][\text{B}] - (k_{-1} + k_3 + k_2[\text{A}])[\text{C}] \quad (2.157)$$

so

$$[\text{C}] \stackrel{\text{SSA}}{\approx} \frac{k_1[\text{A}][\text{B}]}{k_{-1} + k_3 + k_2[\text{A}]} \quad (2.158)$$

Now

$$\frac{d[\text{D}]}{dt} = k_2[\text{A}][\text{C}] + k_3[\text{C}] \quad (2.159)$$

$$= \frac{k_1 k_2 [\text{A}]^2 [\text{B}]}{k_{-1} + k_3 + k_2 [\text{A}]} + \frac{k_1 k_3 [\text{A}] [\text{B}]}{k_{-1} + k_3 + k_2 [\text{A}]} \quad (2.160)$$

In the small [A] limit $k_2[A] \ll k_{-1} + k_3$, giving

$$\text{rate} = \left(\frac{k_1 k_2}{k_{-1} + k_3} \right) [A]^2 [B] + \left(\frac{k_1 k_3}{k_{-1} + k_3} \right) [A] [B] \quad (2.161)$$

and we correctly interpret that there are two important transition states with compositions A_2B and AB .

In the large [A] limit, $k_2[A] \gg k_{-1} + k_3$, so

$$\text{rate} = k_1 [A] [B] + \frac{k_1 k_3}{k_2} [B] \quad (2.162)$$

In the large [A] limit the first term must dominate. We can manipulate the expression to show that explicitly:

$$k_2 \cdot \text{rate} = k_1 k_2 [A] [B] + k_1 k_3 [B] \quad (2.163)$$

$$= k_1 [B] (k_2 [A] + k_3) \quad (2.164)$$

$$\approx k_1 [B] k_2 [A] \quad (\text{from large [A] assumption}) \quad (2.165)$$

$$\text{rate} \approx k_1 [A] [B] \quad (2.166)$$

In this limit the first step has become rate controlling and the k_3 step is unimportant. The relevant T.S. is the AB collision complex.

3. A sum of n terms in the denominator implies a succession of at least n steps; all but the last of them must be reversible.



$$-\frac{d[\text{Tl}^{3+}]}{dt} = \frac{k[\text{Fe}^{2+}]^2[\text{Tl}^{3+}]}{[\text{Fe}^{2+}] + k'[\text{Fe}^{3+}]} \quad (2.168)$$

At low product concentration ($[\text{Fe}^{2+}] \gg k'[\text{Fe}^{3+}]$), we have $\text{rate} = k[\text{Fe}^{2+}]^2[\text{Tl}^{3+}]$.

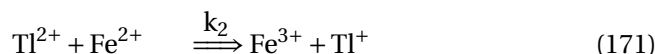
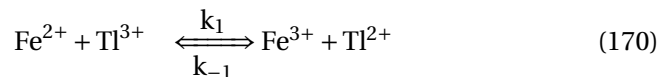
At high product concentration,

$$\text{rate} = \frac{k}{k'} \frac{[\text{Fe}^{2+}]^2[\text{Tl}^{3+}]}{[\text{Fe}^{3+}]} \quad (2.169)$$

With 2 terms in the denominator, we expect two successive transition states. Their compositions (but not order of occurrence) are obtained from the limiting cases where one or the other term dominates. In this example they have compositions $(\text{FeTl})^{5+}$ and $(\text{FeTl})^{4+}$.

4. Species appearing as single terms in the denominator of a rate expression are produced in steps prior to the RCS.

In the last example we postulate that under high concentrations of Fe^{3+} , it is a product in the first of the two steps. The two reactants have total charge +5, so try this mechanism:



The second step has TS composition $(\text{FeTl})^{4+}$, as required. Apply SSA to Tl^{2+} :

$$\frac{d[\text{Tl}^{2+}]}{dt} = k_1[\text{Fe}^{2+}][\text{Tl}^{3+}] - [\text{Tl}^{2+}](k_{-1}[\text{Fe}^{3+}] + k_2[\text{Fe}^{2+}]) \quad (2.172)$$

so

$$[\text{Tl}^{2+}] \stackrel{\text{SSA}}{\approx} \frac{k_1[\text{Fe}^{2+}][\text{Tl}^{3+}]}{k_{-1}[\text{Fe}^{3+}] + k_2[\text{Fe}^{2+}]} = \frac{k[\text{Fe}^{2+}][\text{Tl}^{3+}]}{[\text{Fe}^{3+}] + k'[\text{Fe}^{2+}]} \quad (2.173)$$

$$\text{rate} = k_2[\text{Tl}^{2+}][\text{Fe}^{2+}] = \frac{k_1 k_2 [\text{Fe}^{2+}]^2 [\text{Tl}^{3+}]}{k_{-1}[\text{Fe}^{3+}] + k_2[\text{Fe}^{2+}]} \quad (2.174)$$

$$\text{rate} = \frac{k[\text{Fe}^{2+}]^2 [\text{Tl}^{3+}]}{k'[\text{Fe}^{3+}] + [\text{Fe}^{2+}]} \quad (2.175)$$

where $k = k_1$ and $k' = k_{-1}/k_2$.

So this mechanism agrees with the observed rate law at both low and high concentrations of Fe^{3+} . At high concentrations, the first step becomes a rapid prior equilibrium. Large concentrations of Fe^{3+} drive the concentration of Tl^{2+} down and reduce the rate of formation of product.

2.6.2 Application of “mechanism rules” to a simple inorganic example

Vanadium ions can be oxidized by Hg^{2+} :

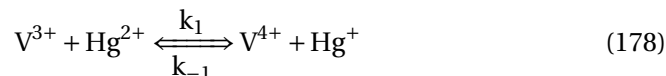


The observed rate law is

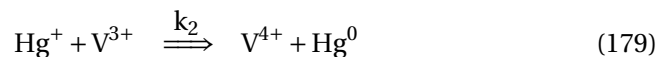
$$-\frac{d[\text{V}^{3+}]}{dt} = \frac{k[\text{V}^{3+}]^2 [\text{Hg}^{2+}]}{k'[\text{V}^{4+}] + [\text{V}^{3+}]} \quad (2.177)$$

Rule 3 tells us to expect at least 2 steps. Rule 1 gives the composition of the two transition states as $(\text{VHg})^{4+}$ and $(\text{VHg})^{5+}$. In the succession of steps required by the rules, all but the last must be reversible.

Since the two reactants can themselves produce one of the two required transition states $((\text{VHg})^{5+})$, it's natural to bring them together as one step:



The Hg^+ product of that reaction can react with another V^{3+} to give the second required transition state. This reaction need not be reversible (but could be). A single, rapid, association reaction between two mercury atoms can complete the mechanism.



Now, let us check to make sure this mechanism gives the correct rate law with reasonable assumptions. The intermediates are Hg^+ and Hg^0 . Applying the SSA to Hg^+ , we find

$$\frac{d[\text{Hg}^+]}{dt} = k_1[\text{V}^{3+}][\text{Hg}^{2+}] - k_{-1}[\text{V}^{4+}][\text{Hg}^+] - k_2[\text{V}^{3+}][\text{Hg}^+] \quad (2.181)$$

$$[\text{Hg}^+] \stackrel{\text{SSA}}{\approx} \frac{k_1[\text{V}^{3+}][\text{Hg}^{2+}]}{k_{-1}[\text{V}^{4+}] + k_2[\text{V}^{3+}]} \quad (2.182)$$

$$-\frac{d[\text{V}^{3+}]}{dt} \stackrel{\text{SSA}}{\approx} k_1[\text{V}^{3+}][\text{Hg}^{2+}] - k_{-1}[\text{V}^{4+}][\text{Hg}^+] + k_2[\text{V}^{3+}][\text{Hg}^+] \quad (2.183)$$

$$= k_1[\text{V}^{3+}][\text{Hg}^{2+}] + [\text{Hg}^+](k_2[\text{V}^{3+}] - k_{-1}[\text{V}^{4+}]) \quad (2.184)$$

$$= k_1[\text{V}^{3+}][\text{Hg}^{2+}] + \left(\frac{k_1[\text{V}^{3+}][\text{Hg}^{2+}]}{k_{-1}[\text{V}^{4+}] + k_2[\text{V}^{3+}]} \right) (k_2[\text{V}^{3+}] - k_{-1}[\text{V}^{4+}]) \quad (2.185)$$

$$= k_1[\text{V}^{3+}][\text{Hg}^{2+}] \left(1 + \frac{(k_2[\text{V}^{3+}] - k_{-1}[\text{V}^{4+}])}{k_{-1}[\text{V}^{4+}] + k_2[\text{V}^{3+}]} \right) \quad (2.186)$$

$$= k_1[\text{V}^{3+}][\text{Hg}^{2+}] \left(\frac{2k_2[\text{V}^{3+}]}{k_{-1}[\text{V}^{4+}] + k_2[\text{V}^{3+}]} \right) \quad (2.187)$$

$$= \frac{2k_1[\text{V}^{3+}]^2[\text{Hg}^{2+}]}{\frac{k_{-1}}{k_2}[\text{V}^{4+}] + [\text{V}^{3+}]} \quad (2.188)$$

which is the observed rate law. Note that the rapid, post-RCS reaction of Hg^0 does not enter the rate law. That is the general case: fast reactions that follow the rate controlling step do not appear in the rate law. Another example of that principle was the decomposition rate of N_6 in the bromine-azide reaction; its rate constant does not appear in any of the rate expressions once the steady state approximation has been applied to N_6 .

2.7 Temperature Dependence of Rates

2.7.1 Arrhenius equation

Most reactions go faster with increasing temperature. An equation often used to describe the T dependence is the Arrhenius equation,

$$k = Ae^{-E_a/RT} \quad (2.189)$$

The Arrhenius equation is neither exact nor universal, but it describes many reactions tolerably well over a modest temperature range, and it contains elements of the correct physics. A and E_a should not be regarded as having precise physical significance in most cases. For elementary reactions, some theories of kinetics do ascribe precise meanings to them. Generally, you should regard E_a as providing a rough estimate of the “reaction barrier”, the height of the energy hill the reactants must climb over on their way to forming products. The activation energy E_a also specifies how sensitive the reaction rate is to temperature; the rate of a reaction will change very strongly with T if E_a is large, and will be relatively insensitive to T if E_a is small. For most reactions E_a is substantially larger than RT .

Figure 2.8 shows the behavior predicted by the Arrhenius equation for the two common plots, k vs. T and $\ln(k)$ vs. $1/T$.

The “classical” method of finding A and E_a is to plot $\ln(k)$ vs. $1/T$ for a series of rate coefficients measured at different T , and get E_a and A from the slope and intercept. Both that method and the more modern nonlinear fit directly to the Arrhenius equation suffer from heavy correlations: The same data can be fit equally well by many different A/E_a pairs, so it is not possible to determine either value very precisely. These correlations occur because the data are taken over a fairly narrow range of T , and long extrapolations are necessary, as appears in the right panel of Figure 2.8.

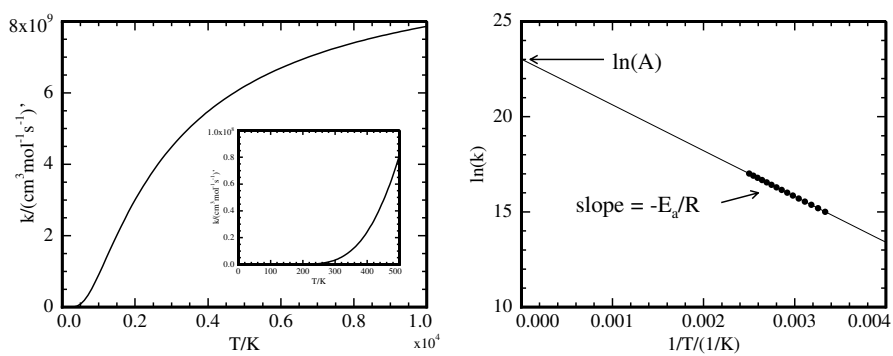


Figure 2.8: Two plots of rate coefficients for a reaction with $A = 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_a = 20 \text{ kJ/mol}$.

Chapter 3

Real gases

3.1 $P - V$ isotherms and the critical point

If you put some gas into a piston-and-cylinder apparatus and slowly push the piston in, holding the apparatus at a constant temperature, the pressure increases—you feel more and more resistance—as you reduce the volume. At some point, the pressure suddenly stops increasing, and you can move the piston in quite far without increasing your pushing force at all. Finally, there is a sudden change, and you find that pushing the piston in any farther requires a very high force. See Figure 3.1 for an illustration.

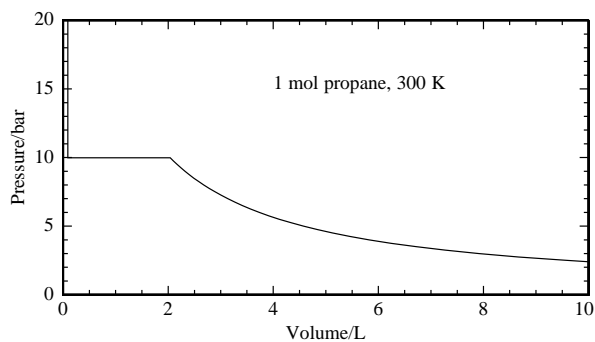


Figure 3.1: The P — V isotherm for propane below the critical temperature.

What is happening? At first, all the material is gas; during that time, it behaves approximately according to the ideal gas law, and the pressure (thus the force pushing against the piston) goes up as the inverse of the volume. Then at some

point—when the pressure has reached the *vapor pressure* of the liquid at the experimental temperature—the gas begins to condense, and both liquid and vapor exist in the cylinder. The pressure remains at exactly this pressure until all the gas has been liquefied. At that point, the cylinder contains only liquid, and compressing this liquid further requires very high pressures.

What happens if you raise the temperature and repeat the experiment? You find that the “flat” section of the trace, where the liquification occurs, appears at higher pressure; you would have expected that, since you know that the vapor pressure increases with temperature. The liquification therefore begins at a smaller total volume than it did before. The point at which you have completely liquified the sample appears at slightly higher volume than before (because liquids expand with increasing temperature). So the total volume range over which you have liquid and gas together goes down at higher temperature.

As you raise the temperature more, the total volume range over which you have both liquid and gas in the cylinder gets smaller and smaller, until finally you find that above a certain temperature you never see both liquid and gas in the cylinder! You compress and compress, and the density goes higher and higher until it equals the liquid density, but you never see the phase change! The temperature at which the liquid-vapor phase change disappears is called the *critical temperature* T_c . Look at Figure 3.2 to see the accurately plotted behavior of the isotherms for propane.

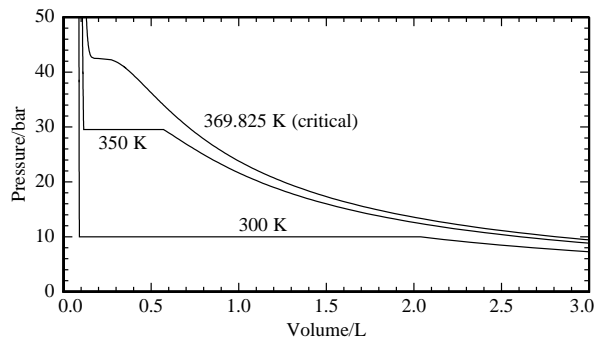


Figure 3.2: Isotherms of a pure substance (propane). Above the critical temperature there are no “corners”; the curve decreases monotonically.

It is obvious from this description that the ideal gas law does not apply to everything; if it did, the pressure would keep following that $1/V$ curve forever. But even in the portion of the curve where only gas exists, the ideal gas law is not fol-

lowed exactly. At intermediate and high densities, intermolecular forces become important, and the pressure deviates from the ideal gas prediction. Sometimes these deviations are large: factors of two or three (at several hundred bar pressure) are common. One way to think about such behavior is to try to devise “improved” gas laws that give more accurate descriptions of the $P - V - T$ behavior. There are two prices to be paid: one, the equations relating P , V , and T will be more complicated, and two, the same equation will not work for all gases. We will need to have *parameters* that can be changed to match the gas in question.

3.2 The van der Waals equation

One of the first, and still the most widely known, equations for real gases is the *van der Waals equation*, developed in 1873. It applies two corrections to the ideal gas law. First, it recognizes that the molecules themselves occupy some volume, so that the volume a single molecule has to fly around in is not the total volume of the container, but the volume of the container minus the volume occupied by all the other molecules. Second, it recognizes that the molecules have some attractive forces between them, that these attractive forces will diminish as the molecules get farther apart, and that their net effect will be to reduce the pressure. The *van der Waals equation of state* is

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \quad (3.1)$$

The numbers a and b are different for each gas; a , which must have units of (pressure)(volume/mole)², accounts for the attractive forces, and b , with units volume/mole, accounts for the volume occupied by the molecules. The attractive term $-a(n/V)^2$, which reduces the pressure, gets smaller as the density decreases, as you expect.

Table 7.4 in Appendix A of E&R gives van der Waals constants a and b for several gases. They can also be estimated from the critical temperature and pressure, given in Table 7.2:

$$a = \frac{27R^2 T_c^2}{64P_c}, \quad (3.2)$$

$$b = \frac{RT_c}{8P_c}. \quad (3.3)$$

b , as you might guess, is similar in magnitude to the volume of one mole of the *liquid* substance. For example, b for water is 30 cm³/mol, while the molar volume of liquid water is 18 cm³/mol. b for benzene is 115 cm³/mol; the molar volume of liquid benzene is 89 cm³/mol.

You usually see the van der Waals equation written in terms of the molar volume $V_m = V/n$:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (3.4)$$

V_m is the volume occupied by one mole of gas; the higher V_m , the lower the density and the less important intermolecular forces will be. In the limit of low densities (that is, large molar volumes), the gas behavior approaches that of an ideal gas. This is easy to see in the van der Waals equation: as V_m gets large, it dominates over b in the denominator of the first term, and makes the second term become small; the equation then reduces to the ideal gas law $P = RT/V_m$.

3.2.1 Critical behavior in the van der Waals equation

To what extent does the van der Waals equation describe condensation and critical behavior? The subcritical isotherms in Figure 3.2 have sharp corners at the onset and completion of condensation; no smooth polynomial function can have corners like that, because polynomial functions have continuous derivatives. So we cannot expect the van der Waals equation to reproduce the isotherms exactly. But it does show critical behavior.

Figure 3.3 shows isotherms calculated from the van der Waals equation using the constants for CO_2 ($a = 3.640 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 0.04267 \text{ L mol}^{-1}$.) At temperatures below the critical temperature T_c , the curves show “loops” (oscillations) in the region that corresponds to condensation. There is a technique, called the “Maxwell construction”, for replacing these oscillations with flat lines, to generate isotherms that look more like the real thing. (E&R describe this trick at the end of section 7.2.) As temperature increases, the loops diminish in amplitude, until finally they disappear; at one particular temperature, the curve has a slope of exactly zero at one particular molar volume, and negative slope everywhere else. That’s the critical temperature T_c . At temperatures above T_c the van der Waals isotherms qualitatively resemble the experimental ones.

3.2.2 Accuracy of the van der Waals equation

To quote Levine’s physical chemistry book: “The van der Waals equation is a major improvement over the ideal-gas equation but is unsatisfactory at very high pressures and its overall accuracy is mediocre.” With it you can estimate properties of dense gases with accuracies much better than the ideal gas law, but you should not expect few-percent accuracy.

There are several other equations of state commonly used for dense gases. Some use two adjustable parameters, just as the van der Waals equation does;

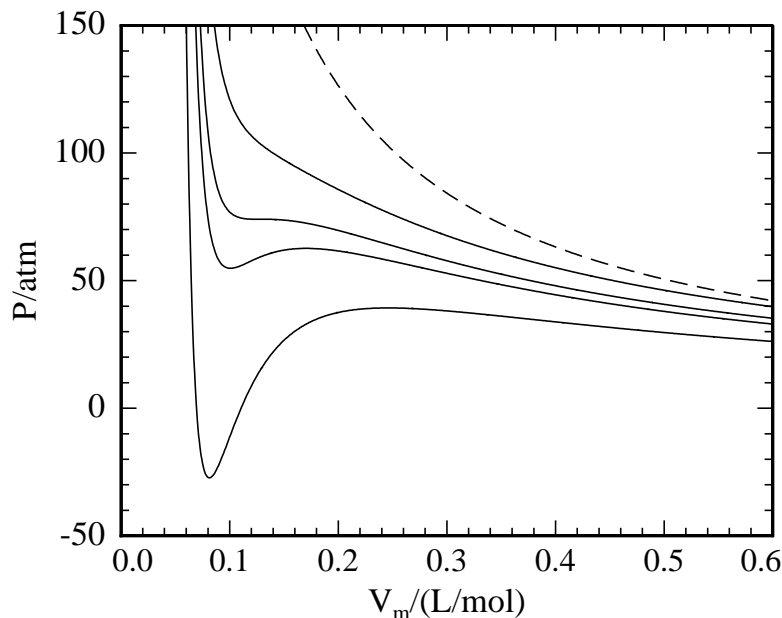


Figure 3.3: Isotherms for CO_2 from the van der Waals equation. From the bottom, the curves represent isotherms at 246.3, 292.5, 307.9, and 338.7 K, which represent, respectively, 0.8, 0.95, 1.0, and 1.1 times T_c^{vdw} . The dashed line gives the ideal gas isotherm at 307.9 K.

some use more parameters in hopes of higher accuracy at the cost of more complication; and one, the *virial equation of state*, replaces the constants for each gas with functions of temperature, giving an effectively infinite number of adjustable parameters. We will consider two of these.

3.3 The Redlich-Kwong equation

A two-parameter equation that is more accurate than the van der Waals equation was developed by Redlich and Kwong (*Chem. Rev.* **44**, 233 (1949)). This equation treats the molecular excluded volume in the same way the van der Waals equation does, but uses a different approach to the effect of the attractive interactions. The Redlich-Kwong equation is

$$P = \frac{RT}{V_m - B} - \frac{A}{V_m(V_m + B)T^{1/2}} \quad (3.5)$$

The Redlich-Kwong A and B are not the same as the corresponding parameters in the van der Waals equation (even the units of A are different.) The equations to estimate them from critical data are

$$A = \frac{R^2 T_c^{5/2}}{9P_c(2^{1/3} - 1)} \quad (3.6)$$

$$B = \frac{(2^{1/3} - 1)RT_c}{3P_c} \quad (3.7)$$

Like the van der Waals equation (and for the same reasons), the Redlich-Kwong equation shows oscillations in the condensation region of a $P-V$ isotherm. Its accuracy in the gas and supercritical regions is much better than the van der Waals equation, and it even describes compression of some liquids fairly well. It is very widely used, especially in engineering.

There are about ten different general-purpose equations of state that are used occasionally for dense gases, with numbers of parameters ranging from two to around six. Many (hundreds!) more equations of state have been developed for particular pressure and temperature ranges for particular sets of gases. This game of find-a-better-analytic-equation-of-state is a classic example of empirical model-building: trying to model complicated observed behavior with a simple equation of a few adjustable parameters, relying on underlying physical understanding of the important processes seasoned with curve-fitting against real data.

3.4 The virial equation

The granddaddy of real-gas equations of state is the *virial equation of state*, which is a Taylor series expansion of the deviations from ideal gas behavior in the variable $1/V_m$. The expansion is made separately at each temperature. The virial equation is most often written as

$$PV_m = RT \left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots \right) \quad (3.8)$$

The function $B(T)$ is called the second virial coefficient, $C(T)$ is the third virial coefficient, and so on. Notice that if all the virial coefficients are zero, the virial equation turns into the ideal gas equation. The temperature-dependent coefficients therefore tell us something about the interactions between the molecules. $B(T)$ describes the interactions between pairs of molecules; $C(T)$ describes “three-body” interactions, and so on.

$B(T)$ has been measured (at dozens of temperatures) for hundreds of gases; $C(T)$ is known for a few dozen gases; only a few $D(T)$ values have been measured. At low to medium pressures, $B(T)$ alone is sufficient for accuracies better than one percent in most cases.

At low temperature and low density, the attractive interactions between the molecules are more important than the repulsions, so that the pressure in a sample of gas is less than the ideal gas law predicts; $B(T)$ is therefore negative at low temperatures, and drops steeply at very low T . At high temperature, the molecules are moving fast enough that they do not really feel the weak attractive forces, and they act more or less like hard spheres; $B(T)$ therefore reaches a value roughly like the liquid density at high T and decreases very slowly at very high T .

It is possible, through statistical mechanics, to calculate the virial coefficients if the intermolecular potential is known. For spherical particles (not necessarily hard spheres: this works for realistic potentials) the formula is

$$B(T) = -2\pi N_A \int_0^\infty \left(\exp\left(\frac{-v(r)}{kT}\right) - 1 \right) r^2 dr \quad (3.9)$$

where $v(r)$ is the intermolecular potential function. For realistic $v(r)$ this integration usually has to be done numerically, but there are good techniques for doing so and the calculation is not very hard. (I've done it many times, and have computer programs available for the job.) This makes a nice test of a model potential function, since $B(T)$ can be determined experimentally to within a few percent. (Actually, Eq. (3.9) is approximate: it is the prediction of classical mechanics, which is usually very good at room temperature and above but is inaccurate at low temperature. There are quantum corrections, also not hard to calculate, which must be used at low temperatures. See Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids*, for details.)

Figure 3.4 shows a special kind of virial coefficient, called an interaction virial coefficient, for H_2 -CO interactions. (This figure is taken from a paper by Jennifer Gottfried and me.) The shape of $B(T)$ it shows is typical. In addition to the experimental data, three different sets of $B(T)$ values calculated from theoretical potential energy functions $v(r)$ are shown. You can see that good experimental data are capable of distinguishing between different theoretical models.

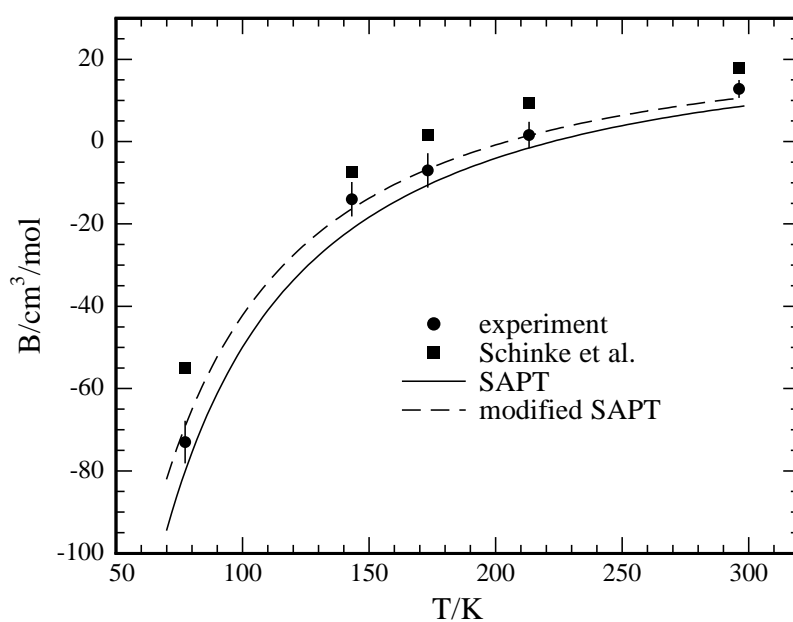


Figure 3.4: Interaction second virial coefficients for H_2 - CO . The three theoretical $B(T)$ come from a 1985 calculation (Schinke et al.), a 1998 calculation (SAPT), and that same 1998 calculation but scaled to make the attractive well about 5% less deep.

Chapter 4

First Law of thermodynamics

4.1 Introduction

We already calculated the average kinetic energy of the particles in an ideal gas: $\langle \varepsilon_{\text{tr}} \rangle = 3kT/2$. If the particles have no other kinds of energy (they cannot rotate, for example), then we can regard the sum of all the particles' kinetic energies as the total energy of the gas. We can do anything at all to this sample of gas, but if in the end, we have the same number of particles and we bring them back to the same temperature, the total energy will be the same. This total energy, which is generally called the *internal energy* of the gas, is a *state function*: it depends only on the present condition of the gas sample and not on its previous history.

The internal energy is an extensive property: if we divide the sample in half (by putting a partition in the container, for example), each half has half the internal energy the original sample had. The volume of the gas is another extensive property. The pressure and temperature, though, are not extensive: if we divide the sample of gas in half, each half has the same pressure and temperature as the original sample. We say that pressure and temperature are intensive properties. Internal energy, pressure, temperature, and volume are all state functions.

How might we increase the internal energy of the gas? Obviously, we must increase its temperature (or the number of gas molecules.) All the myriad ways of increasing the sample's temperature fall into two great categories: we can either *heat* the gas, or we can do *work* on the gas.

Heating the gas is easy: we place the gas into a container whose walls are "thermally conductive", then we place that container in contact with some object whose temperature is higher than that of the gas (for instance, a beaker of hot water, or an oven of hot air), and we wait. After a while, the gas and its container will have warmed up, and the formerly warm object will have cooled off, until

the two temperatures are the same. At that point, the two objects have reached thermal equilibrium and there will be no more energy transfer. This procedure effectively provides us with a definition of heat: an energy flow caused by a difference in temperature between two objects.

Doing work on the gas is also simple: we put the gas into a container whose walls do not conduct heat, but whose volume is adjustable (for example, a syringe with vacuum-jacket walls). Then we compress the gas. The work we do in this process is just the force applied times the distance over which the force operates; when the gas pressure is P , if the piston has face area A and we push it through a small distance dx , the work we do is $dw = PA dx$. Adding those small amounts of work up over some finite change in volume gives the total work done on the gas. Compressing the gas in this way increases its temperature.

The first law of thermodynamics, which is essentially a statement of conservation of energy, says that the change in total energy of any closed system during any process is equal to the sum of the heat flow into the system, q , and the work done on the system, w :

$$\Delta E = q + w \quad (4.1)$$

Calling the system *closed* means that no molecules can enter or leave.

In most problems of interest to chemists (though not to chemical engineers, who deal all the time with stuff flowing through pipes) the sample has no important *external* energy (overall kinetic or potential energy), so the total energy E can be replaced with the internal energy U to give

$$\Delta U = q + w \quad (4.2)$$

Contrary to popular usage, *heat* in thermodynamics is not something that a sample *contains*; instead, heat is a process, an energy transfer between two things because of a temperature difference. It makes no sense in thermodynamics to ask “How much heat does 3.4 g of iron contain at 343 K and one bar pressure?” Heat is not a state function. Even so, the old caloric theory, which regarded heat as a fluid that moved from one object to another (and was conserved!), is deeply ingrained into our language and produces the phrases “a container whose walls conduct heat”, “heat capacity”, “heat flow”, and so on.

Early data that ultimately supported a serious attack on the caloric theory were provided in 1798 by Count Rumford, an expatriate American who lived in Massachusetts but supported England in the American Revolution and moved to Europe after the war. He was in charge of the Bavarian Army, and recognized that enormous amounts of heat were produced during the boring of cannons. This production of heat contradicted the prevailing idea of conservation of heat. In fact he measured that a cannon borer, driven by one horse for 2.5 hours, produced enough heat to raise 27 pounds of water from ice-cold to the boiling point.

4.2 Work against constant force

As an example of a simple calculation using the first law, consider the following problem:

A sample of ideal gas at a pressure of 2 bar and at room temperature is contained in a syringe. The cross-sectional area of the plunger is 4 cm^2 , and the external pressure is 1 bar. (The weight of the plunger is negligible compared to the force of the atmosphere acting on the plunger.) We let the plunger rise slowly (it rises because of the higher pressure inside). We let it rise by 2 cm, then stop it. The gas inside is now cooled; as it warms back up to room temperature, how much heat flows from the room into the gas?

Because the gas is ideal, its internal energy depends only on its temperature and not its volume (since attractive and repulsive forces between the molecules, which would depend on the volume, are zero in an ideal gas.) In this problem the gas ends at the same temperature as it began, so its internal energy is unchanged ($\Delta U = 0$). Also, the force against which it is pushing is constant, so we can calculate the work the gas does with the formula $w = -F\Delta x$.

The force against which the plunger must work is the force of the external atmosphere, that is,

$$F_{\text{ext}} = P_{\text{ext}}A, \quad (4.3)$$

where P_{ext} is the external atmospheric pressure and A is the area of the plunger face. Plugging in the values and changing units appropriately, we find $F_{\text{ext}} = (10^5 \text{ Pa})(4 \times 10^{-4} \text{ m}^2) = 40 \text{ N}$, so that $w = -F\Delta x = -(40 \text{ N})(0.02 \text{ m}) = -0.80 \text{ J}$. I have used the convention that work done *on* the system is positive, while work done *by* the system on the surroundings is negative; this convention is the most common one in modern chemistry and is adopted by all recent textbooks. (Older books, or books by engineers, sometimes switch the sign on w so that work done *by* the system on the surroundings is positive. Should you encounter such a text, be careful with the signs!)

Since $\Delta U = 0$, we have $q = -w$, and 0.802 J of energy flows as heat between the room and the gas to bring it back to room temperature.

4.3 General PV work

In the piston-and-cylinder apparatus, the work done against external pressure P_{ext} is

$$dw = -P_{\text{ext}}A dx = -P_{\text{ext}} dV \quad (4.4)$$

where dV is the change in volume. We can regard any expansion against an external pressure, independent of the shape of the container, as a collection of

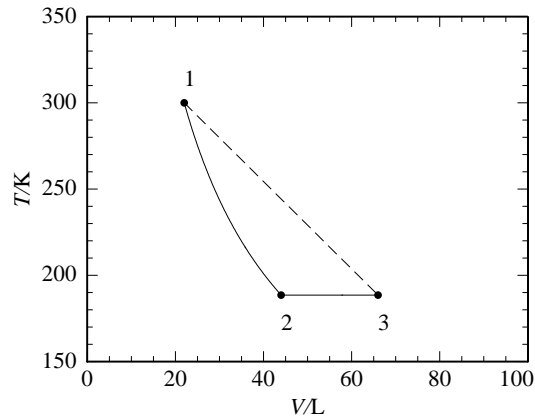


Figure 4.1: Work done in expansion of the system. If the system moves in a cyclic way, eventually returning to point A, the work done is given by the area enclosed within the cycle on the diagram.

small pistons, and the overall work done in any expansion is still

$$dw = -P_{\text{ext}} dV. \quad (4.5)$$

If the volume change is positive (the system gets bigger), the work is negative; this agrees with our convention that work done *on* the system is positive.

4.3.1 Expansion against constant external pressure

We have examined this case already: if the external pressure is constant, then we have

$$w = - \int_{V_1}^{V_2} P_{\text{ext}} dV = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}}\Delta V. \quad (4.6)$$

We did not know, or care, what the pressure of the gas was; it is only the *external* pressure, against which the system expands, that matters. That is still true even if the external pressure changes during the expansion, so long as we know what it is; that is,

$$w = - \int_{V_1}^{V_2} P_{\text{ext}}(V) dV, \quad (4.7)$$

and the work is the area under the curve $P_{\text{ext}}(V)$ on a $P - V$ diagram. Notice (Figure 4.1) that the work depends on what “path” we follow on the diagram. If

we move along path ABC , the work done on the surroundings is larger than if we move along path ADC .

In fact, we can think about recompressing the sample somehow, bringing it back to point A . If we expand along route ABC , we do work w_{ABC} on the surroundings; then to move back along route CDA , we must do work w_{CDA} on the system. The net work we extract from the system (think “steam engine”) is the area between the two curves.

4.4 Reversible processes

It is useful to describe a sort of process in thermodynamics that corresponds to “frictionless” processes in mechanics. The appropriate sort is one that is nearly at equilibrium all the way through. Of course, a system truly at equilibrium (internally and with its surroundings) does not change with time; that is essentially the definition of equilibrium. But, a system very slightly displaced from equilibrium will move; if you change the displacement very slightly in the other direction, the motion will reverse direction. Such a process, held nearly at equilibrium all the way through, is called a *reversible* process in thermodynamics.

As an example, consider our piston and cylinder apparatus expanding against external pressure. If we adjust the external pressure to be exactly equal to the internal pressure, the piston will not move at all. If we then very slightly reduce the external pressure, the piston will move slowly outward; we can stop it, and in fact reverse it, by a very small increase in the external pressure. If we let the piston move outward very slowly, by continuously adjusting the external pressure to be very slightly below the internal pressure, then we are carrying out a *reversible expansion* of the system.

A true reversible expansion is not a practical thing to do, because it takes forever to make a finite change in the volume. Therefore, real devices do not act reversibly. Reversible processes nevertheless play an important role in thermodynamics for several reasons. First, some devices do act very nearly like reversible ones (for instance, many electrochemical processes occur nearly at equilibrium.) Second, and more important, it is often possible to calculate changes in a system’s state functions during some process easily if we assume the process occurs reversibly; since state functions do not depend on paths, we can substitute a reversible change for the real one and get the same answer with less effort. We cannot, of course, use this trick for calculating q or w , since those are not state functions. Third, those (easier) calculations of system properties often reliable limits on the behavior to be expected from real systems. That is, they may provide firm statements of the type “It is not possible to do better than this.”

Example: reversible isothermal expansion of an ideal gas If we allow an ideal gas to expand reversibly, then we know that $P_{\text{ext}} = P$ during the entire expansion; we can therefore replace the external pressure P_{ext} with the system pressure P in the expression for the work. Let us say we allow our system to expand reversibly from state 1, (P_1, V_1, T) to state 2, (P_2, V_2, T) . How much work is done?

We don't know yet. Many different paths could carry the system from state 1 to state 2, and before we can calculate the work we must specify a path. We can do that by specifying T at each point on the path; since V is the independent variable, and n is held constant, the specification of T at each point suffices to uniquely identify a path.

In the reversible *isothermal* expansion, we keep the temperature of the gas constant throughout the expansion (perhaps by immersing the cylinder into a large constant-temperature bath.) Then we have

$$w = - \int_{V_1}^{V_2} P_{\text{ext}}(V) dV \quad (4.8)$$

Since the expansion is reversible we replace P_{ext} with P :

$$= - \int_{V_1}^{V_2} P(V) dV \quad (4.9)$$

$$= - \int_{V_1}^{V_2} \frac{nRT}{V} dV \quad (4.10)$$

$$= -nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad (4.11)$$

$$= -nRT [\ln V]_{V_1}^{V_2} \quad (4.12)$$

$$= -nRT \ln \left(\frac{V_2}{V_1} \right). \quad (4.13)$$

4.5 Enthalpy

For any process at constant volume, if we consider no work other than PV work, then $w = 0$, so that

$$\Delta U = U_2 - U_1 = q_V \quad (4.14)$$

(where the subscript V indicates constant volume.)

If, instead, we carry out a process at constant pressure, then

$$\Delta U = U_2 - U_1 = q_p + w_p = q_p - P(V_2 - V_1), \quad (4.15)$$

so that

$$(U_2 + PV_2) - (U_1 + PV_1) = q_p \quad (4.16)$$

This equation suggests that it might be useful to define a new state function H :

$$H = U + PV \quad (4.17)$$

H is called the *enthalpy*. It is clearly a state function since U , P , and V are all state functions. Now we have

$$H_2 - H_1 = \Delta H = q_p \quad (4.18)$$

The change in enthalpy of a system that undergoes a process at constant pressure is just the heat that enters the system during the process. H , like U and V , is extensive.

4.6 Heat capacities

How does the system temperature change for a given amount of heating? If an amount of heat dq enters the system, the temperature changes by dT and we define the *heat capacity* C from

$$dq = C dT \quad (4.19)$$

or

$$C = \frac{dq}{dT} \quad (4.20)$$

Since other things may happen to the system as it is heated (for instance, it might expand, or its pressure might rise, or it might undergo some chemical reaction), we can expect different temperature changes under different conditions. It is conventional to define two kinds of heat capacities, C_V for the heat capacity when the volume is held constant, and C_p for the heat capacity at constant pressure. Then we have

$$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T} \right)_V \quad (4.21)$$

$$C_p = \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T} \right)_P \quad (4.22)$$

$C_p \geq C_V$ for a given system because some of the heat entering a system at constant pressure can leave in the form of work done on the surroundings. (For

gases the difference is important, while for liquids and solids at ordinary pressures it is negligible.) At constant volume it is not possible to do expansion work on the surroundings, so all the heat that enters serves to increase the system's temperature.

Heat capacity is extensive; if you double the amount of material in your system, you will have to add twice as much heat to get its temperature to change by the same amount. An entire system, even a complicated one, can have a well-defined heat capacity; the system, for example, might be an entire combustion calorimeter, including the sample, the oxygen gas, the steel bomb enclosing the sample and gas, the water surrounding the bomb, and the thermometer.

It is traditional to define intensive heat capacities for pure substances in two ways. One, the *specific heat* (or, more recently, specific heat capacity), is the amount of heat required to raise the temperature of 1 g or 1 kg of a specified substance by 1 K (typically at constant pressure). The other is the *molar heat capacity*, $C_{V,m} = C_V/n$ or $C_{p,m} = C_p/n$, which is the amount of heat required to raise the temperature of one mole of substance by 1 K.

4.6.1 Heat capacities for ideal gases

Let us find the relation between C_V and C_p for an ideal gas. Begin with

$$H = U + PV \quad (4.23)$$

Differentiating with respect to T at constant P gives

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \quad (4.24)$$

and, recognizing the definition Eq. (4.22), we have

$$C_p = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P. \quad (4.25)$$

From the ideal gas law we can evaluate the last term to give

$$C_p = \left(\frac{\partial U}{\partial T}\right)_P + P \frac{nR}{P} \quad (4.26)$$

$$= \left(\frac{\partial U}{\partial T}\right)_P + nR \quad (4.27)$$

Now I must make a qualitative physical argument that we will be able to replace with a more mathematical one in a week or so. For an ideal gas, U represents only

the energy (internal and translational) of individual gas molecules, since there are no intermolecular interactions (and therefore no intermolecular potential energies). Therefore U cannot depend on V or on P ; the distance between the molecules does not change anything about their total energy. U is therefore a function of T only. The same must be true of H , since $H = U + PV$ and PV is a function only of T for an ideal gas. Therefore for an ideal gas

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_P = \frac{dU}{dT}, \quad (4.28)$$

so finally

$$C_p = C_V + nR. \quad (4.29)$$

Thermodynamics does not give us theoretical tools to predict heat capacities; they are quantities that must be measured for each substance. (Statistical mechanics does provide formulas for prediction of heat capacities from molecular properties.) Heat capacities for most substances change with temperature; an exception is that for a monatomic ideal gas, for which we calculated from the kinetic theory of gases that $U = \frac{3}{2}nRT$. We therefore have for a monatomic ideal gas that

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2}nR. \quad (4.30)$$

The heat capacity at constant pressure is therefore

$$C_p = C_V + nR = \frac{5}{2}nR. \quad (4.31)$$

The heat capacity ratio C_p/C_V is traditionally called γ ; it plays an important role in the study of gas dynamics. For a monatomic gas the heat capacity ratio is

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}nR}{\frac{3}{2}nR} = \frac{5}{3}. \quad (4.32)$$

The quantity γ is observable experimentally and is accurately 1.667 for noble gases at low densities.

4.6.2 Reversible adiabatic expansion of an ideal gas

We now have the tools to analyze a reversible *adiabatic* expansion of a gas. We did the reversible isothermal expansion before; the adiabatic expansion is a little harder because the temperature of the gas changes as the expansion goes on.

Adiabatic means no heat flows: $q = 0$, so $\Delta U = w$. We can find two different expressions for dw :

$$dw = -P dV = -\frac{nRT}{V} dV \quad (4.33)$$

$$dw = dU = C_V dT \quad (4.34)$$

Equating those two and dividing by T separates the variables:

$$C_V \frac{dT}{T} = -nR \frac{dV}{V} \quad (4.35)$$

Integrate both sides:

$$\int_{T_1}^{T_2} C_V \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V} \quad (4.36)$$

If we assume that C_V is independent of temperature (true for a monatomic ideal gas, an excellent approximation for many diatomic gases at ordinary temperatures), we can integrate both sides to get

$$C_V \ln \left(\frac{T_2}{T_1} \right) = -nR \ln \left(\frac{V_2}{V_1} \right). \quad (4.37)$$

Now we know how the temperature will change during the expansion. Notice that for an adiabatic expansion ($V_2 > V_1$), the gas cools. Given the initial temperature and volume, and the final volume, you can now find the final temperature; since C_V is constant you then have simply $\Delta U = C_V \Delta T$, and since $q = 0$ the work done by the gas is just $-\Delta U$.

Application: supersonic expansions A common laboratory technique in spectroscopy and collision experiments is to use a reversible, adiabatic expansion from high to low pressure to cool a gas. Let me show an example calculation.

We know for an ideal gas that $C_p = C_V + nR$. We can therefore substitute for nR in Eq. (4.37) to get

$$C_V \ln \left(\frac{T_2}{T_1} \right) = -(C_p - C_V) \ln \left(\frac{V_2}{V_1} \right) \quad (4.38)$$

and writing $C_p/C_V = \gamma$ gives

$$\ln \left(\frac{T_2}{T_1} \right) = (1 - \gamma) \ln \left(\frac{V_2}{V_1} \right) \quad (4.39)$$

It is more convenient in the laboratory to think about the ratio of initial and final pressures in the expansion than the ratio of volumes. For ideal gases,

$$\frac{V_2}{V_1} = \frac{T_2 p_1}{p_2 T_1} \quad (4.40)$$

and substituting for the ratio of volumes gives

$$\ln\left(\frac{T_2}{T_1}\right) = (1 - \gamma) \ln\left(\frac{T_2 p_1}{T_1 p_2}\right). \quad (4.41)$$

Using $a \ln b = \ln(b^a)$ and exponentiating both sides gives

$$\frac{T_2}{T_1} = \left(\frac{T_2 p_1}{T_1 p_2}\right)^{1-\gamma} = \left(\frac{T_1 p_2}{T_2 p_1}\right)^{\gamma-1}, \quad (4.42)$$

and we can gather terms to get

$$\left(\frac{T_2}{T_1}\right)^\gamma = \left(\frac{p_2}{p_1}\right)^{\gamma-1} \quad (4.43)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}. \quad (4.44)$$

In a typical application in the laboratory, a monatomic gas (most often helium or argon: $\gamma = 5/3$) expands from a pressure of about 2 bar and a temperature of 300 K to a pressure of 10^{-2} mbar. We then have

$$\frac{T_2}{T_1} = \left(\frac{10^{-2}}{2000}\right)^{\frac{2/3}{5/3}} = (5 \times 10^{-6})^{2/5} = 0.0076, \quad (4.45)$$

so that the final temperature is $(.0076)(300 \text{ K}) = 2.3 \text{ K}$! This experiment can be carried out in an apparatus that uses a medium-size diffusion pump (20cm throat) and a vacuum chamber perhaps a foot in diameter. One of the most important applications is in spectroscopy of medium-sized molecules; at room temperature their spectra are hopelessly complicated, but at 2 K only a few rotational levels are populated and it is much easier to figure out what is going on.

4.7 Standard enthalpy changes

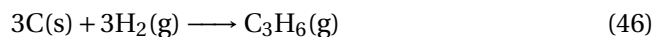
4.7.1 Hess's law and enthalpies of formation

Well before the First Law was known, Hess formulated the *Law of Constant Heat Summation*: ΔU or ΔH for any chemical reaction is independent of the path, and in particular, independent of any intermediate reactions that may occur. (Hess made a real discovery: the heat evolved in most processes was not independent of path, but for chemical reactions carried out at constant pressure, it was!) This means that if you can find any set of reactions that can combine (on paper, even if not in the lab) to transform your reactants to your products, and the ΔH has been measured under some conditions for each, you can figure out ΔH for the reaction you are interested in. The use of Hess's Law is usually covered in general chemistry.

Because of Hess's Law, it is useful to tabulate "standard enthalpies" for specific reactions of many substances; if the reactions are chosen carefully, it will then be possible to calculate enthalpy changes for many other reactions involving those substances. The most widely tabulated standard enthalpy is the *standard enthalpy of formation*, which gives the enthalpy change for the reaction that forms one mole of the substance in question from the constituent elements in their "standard states" (that is, the most stable pure form at the temperature in question.) The enthalpy of formation of any pure element in its standard state at a specified temperature is defined to be zero.

To make such reaction enthalpies truly standard, it is necessary to specify both the pressure and the temperature at which the reaction occurs. The temperature is generally specified explicitly; most enthalpies of formation are given at 298.15 K, but values are sometimes available at other temperatures. For many years the standard pressure was 1 atm, but in 1982 the standard changed to 1 bar and most tables now use that value. The change in standard pressure really only matters for reactions involving gases.

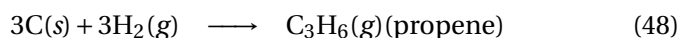
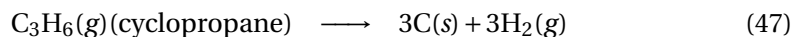
So, for example, the standard enthalpy of formation of cyclopropane at 298.15 K is the heat absorbed by the chemical system when the reaction



is carried out at 1 bar pressure and 298.15 K. The symbol for this quantity is $\Delta_f H_{298.15}^\circ$. The Δ indicates a change in a state function. (It is important, when looking at tables of thermodynamic functions, to always keep in mind what kind of change the tables refer to!) The subscript f indicates what kind of change: in this case, it is a formation reaction. H , of course, tells you what quantity is being monitored during the change: the enthalpy. The superscript $^\circ$ (some books use a

degree symbol instead) indicates “standard state”, which is some agreed-upon set of conditions that together with the temperature fix the state of the system. For systems whose chemical composition is otherwise specified (as here: we are considering one mole of cyclopropene being formed from its elements), the only condition implied by the standard-state symbol is the standard pressure. Finally, the temperature is listed as a subscript. The older practice (now obsolete, but followed by some authors anyway) was to attach the subscript *f* to the *H* rather than to the Δ .

Example Let us evaluate the enthalpy change in the isomerization of cyclopropane to propene at 298 K and 1 bar pressure. We can construct the reaction from two formation reactions, as follows:



Eq. (48) is the formation reaction for propene; the corresponding enthalpy change is the enthalpy of formation (also called heat of formation) of propene, 20.41 kJ/mol. Eq. (47) is the reverse of the formation reaction of cyclopropene; the enthalpy of formation of cyclopropene is 53.3 kJ/mol, so the enthalpy change in Eq. (47) is -53.3 kJ/mol. The overall enthalpy change is the sum of those two, or -32.9 kJ/mol. The negative sign indicates that heat is released when cyclopropane isomerizes to propene under those conditions; the reaction is exothermic.

4.7.2 Reactions at nonstandard temperatures

What happens if you want the enthalpy change for a reaction at some temperature other than 298.15 K? You must think of your reaction as occurring in a series of steps, calculate the enthalpy change for each, then sum them up to get the overall enthalpy change. For example, if we wanted to know the enthalpy change for the isomerization of cyclopropane to propene at 350 K and 1 bar pressure, the following series of steps would be useful:

1. Cool cyclopropane from 350 K to 298.15 K under constant pressure of 1 bar. The enthalpy change for this process is

$$\Delta H = \int_{350}^{298.15} C_p^c dT \quad (4.50)$$

where C_p^c is the constant-pressure heat capacity of cyclopropane.

2. Convert cyclopropane to propene at 298.15 K at 1 bar; the enthalpy change for that process we already worked out to be $\Delta_r H^\circ = -32.9 \text{ kJ/mol}$.
3. Heat propene from 298.15 to 350 K. The enthalpy change for that process is

$$\Delta H = \int_{298.15}^{350} C_p^{\text{p}} dT \quad (4.51)$$

where in this case C_p^{p} is the heat capacity of propene.

To carry out this program we need to know the two heat capacities as functions of temperature. The NIST WebBook gives the data shown in Table 4.1; it is plotted in Figure 4.2.

When I look at the heat capacity data on a plot, it seems like a linear fit will be perfectly reasonable; such a fit is shown, for both compounds. With slopes and intercepts from those fits it is possible to carry out the integrations corresponding to the heating and cooling stages. Note that it is really the difference between the two heat capacities we need:

$$\Delta H = \int_{350}^{298.15} C_p^{\text{c}} dT + \Delta_r H_{298.15}^\circ + \int_{298.15}^{350} C_p^{\text{p}} dT \quad (4.52)$$

$$= \Delta_r H_{298.15}^\circ + \int_{298.15}^{350} (C_p^{\text{p}} - C_p^{\text{c}}) dT \quad (4.53)$$

$$= \Delta_r H_{298.15}^\circ + \int_{298.15}^{350} \Delta C_p dT \quad (4.54)$$

Writing $C_p^{\text{c}} = a + bT$, $C_p^{\text{p}} = c + dT$, I have $\Delta C_p = (c - a) + (d - b)T$, so that

$$\Delta H = \Delta_r H_{298.15}^\circ + \int_{298.15}^{350} \Delta C_p dT \quad (4.55)$$

$$= \Delta_r H_{298.15}^\circ + \int_{298.15}^{350} (c - a) + (d - b)T dT \quad (4.56)$$

$$= \Delta_r H_{298.15}^\circ + [(c - a)T + (d - b)T^2]_{298.15}^{350} \quad (4.57)$$

$$= \Delta_r H_{298.15}^\circ + [(17.19 - (-4.16))T + (.158 - .200)T^2]_{298.15}^{350} \quad (4.58)$$

$$= -32.9 \text{ kJ/mol} - 304 \text{ J/mol} \quad (4.59)$$

$$= -33.2 \text{ kJ/mol} \quad (4.60)$$

You should be able to see how to take into account other kinds of processes that relate your reaction conditions of interest to the standard conditions. If you want to carry out the reaction at some pressure other than one bar, you can evaluate the enthalpy changes for an isothermal, reversible compression or

Table 4.1 Heat capacity data for cyclopropane and propene, from the NIST Chemistry WebBook (webbook.nist.gov/chemistry).

T/K	C_p (propene)/J/mol	T/K	C_p (cyclopropane)/J/mol
298.15	63.79	298.15	55.6
299.33	64.73	300.48	56.48
300.	64.71	313.9	59.29
320.	67.89	316.7	59.27
323.15	67.88	325.1	60.90
333.86	70.04	332.8	62.17
340.	71.03	333.70	63.18
348.15	71.78	338.9	64.27
360.	74.13	339.6	63.26
		368.46	70.17

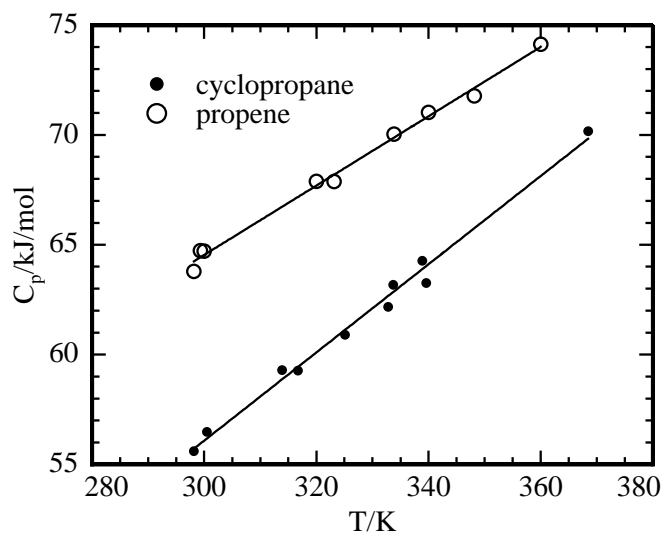


Figure 4.2: Heat capacity data from Table 4.1. Lines are fitted through both sets; for cyclopropane, the slope is 0.200J/mol K and the intercept is -4.16J/mol , while for propene the slope is 0.158J/mol K and the intercept is 17.19J/mol .

expansion before and after the reaction. If there is a phase change in reactants or products at a temperature intermediate between your reaction temperature and the known reaction enthalpy, you must include the enthalpy for that phase change (using $\Delta_{\text{fus}}H$ or $\Delta_{\text{vap}}H$) in your thermodynamic path. The whole game is to be able to identify *some* path that will get you from your reactants at the desired conditions to products at the desired conditions, and for which you are able to evaluate the enthalpy changes for each step. Because H is a state function, it does not matter whether the path you choose is related to the actual experimental path at all.

4.7.3 Other kinds of standard enthalpy changes

Many processes other than “formation from elements” also have standard enthalpy changes that can be looked up. You have already met the standard enthalpy changes for phase changes, $\Delta_{\text{fus}}H^\circ$ and $\Delta_{\text{vap}}H^\circ$. For sublimation there is also a $\Delta_{\text{sub}}H^\circ$. In all cases, these values give the amount of heat absorbed by one mole of the substance while it undergoes a phase change at constant temperature and pressure (typically, though by no means always, the transition temperature at 1 bar pressure).

One of the most important standard enthalpy changes is that for *combustion*, not for any theoretical reason but because enthalpies of combustion $\Delta_c H^\circ$ are relatively easy to measure for many substances. In fact, it is nearly impossible to carry out many “formation” reactions cleanly. Therefore, most enthalpies of formation that appear in tables have in fact been determined by measuring the heats of combustion of the reactants and products and using Hess’s Law to calculate the heats of formation.

Chapter 5

Mathematical interlude

5.1 Properties of partial derivatives

For many kinds of thermodynamic calculations, it is useful to be able to manipulate partial derivatives easily. In this section I will give, without proof, several formulas that can be used in such manipulations. Most of these are listed in Appendix B.6 of E&R.

Order of partial differentiation Most functions we will be concerned with will have continuous derivatives. For such functions, a “mixed second partial derivative” can be taken in either order:

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial f(x, y)}{\partial x} \right) \right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial f(x, y)}{\partial y} \right) \right)_y. \quad (5.1)$$

That is, if you need to differentiate something with respect to two variables, you can switch the order of differentiation if you need to.

Chain rule The chain rule works for partial derivatives just as with ordinary derivatives, so long as the same variable is held constant for all the terms:

$$\left(\frac{\partial f}{\partial z} \right)_x = \left(\frac{\partial f}{\partial y} \right)_x \left(\frac{\partial y}{\partial z} \right)_x \quad (5.2)$$

For example,

$$\left(\frac{\partial p}{\partial V} \right)_T = \left(\frac{\partial p}{\partial V_m} \right)_T \left(\frac{\partial V_m}{\partial V} \right)_T = \frac{1}{n} \left(\frac{\partial p}{\partial V_m} \right)_T. \quad (5.3)$$

Inversion rule Just as for regular derivatives, you can switch the “differentiator” and the “differentiatee” if you invert the derivative (this is the great insight of the Leibniz notation for derivatives:)

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z} \quad (5.4)$$

This property is often very handy when you work with real gases. The van der Waals equation is difficult to write in the form $V_m = f(p, T)$, but you sometimes need derivatives of V_m with respect to the other variables. Let us calculate the *isothermal compressibility* of a van der Waals gas:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad (5.5)$$

$$= -\frac{1}{V} \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} \quad (5.6)$$

The van der Waals equation is most conveniently written in terms of V_m , so apply the chain rule:

$$= -\frac{1}{V} \frac{1}{\left(\frac{\partial p}{\partial V_m}\right)_T \left(\frac{\partial V_m}{\partial V}\right)_T} \quad (5.7)$$

$$= -\frac{1}{V} \frac{1}{\left(\frac{\partial p}{\partial V_m}\right)_T \frac{1}{n}} \quad (5.8)$$

$$= -\frac{1}{V_m} \frac{1}{\left(\frac{\partial p}{\partial V_m}\right)_T} \quad (5.9)$$

The remaining partial derivative can be evaluated easily from the van der Waals equation; evaluating it and rearranging gives

$$\kappa_T = \frac{V_m^2 (V_m - b)^2}{RTV_m^3 - 2a(V_m - b)^2} \quad (5.10)$$

Shifting the constant quantity If you need to change which of several variables is held constant during a partial differentiation, you must add a correction term:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \quad (5.11)$$

We already had an opportunity to apply this rule, though we swept it under the rug. Eq. (4.27) was

$$C_p = \left(\frac{\partial U}{\partial T} \right)_P + nR$$

and I claimed that the partial derivative was equal to $(\partial U/\partial T)_V$ because U depends on neither P nor V . Let's use the shift rule to show that explicitly. Here U plays the role of f , T plays the role of x , P plays the role of z , and V plays the role of y . So we have

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (5.12)$$

$$= \left(\frac{\partial U}{\partial T} \right)_V + 0 \left(\frac{\partial V}{\partial T} \right)_P \quad (5.13)$$

because U does not depend on V , so $(\partial U/\partial V)_T = 0$. So we get

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V \quad (5.14)$$

as I claimed before.

Permutation rule This rule is a version of the chain rule that lets the constant quantities shift. Note the “permutation” that occurs among the numerator, denominator, and subscript, and also note the (surprising, at first) minus sign.

$$\left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \quad (5.15)$$

Real gases have nonzero *Joule-Thompson coefficients*, μ :

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H. \quad (5.16)$$

A quantity that is easier to measure than μ is the isothermal Joule-Thompson coefficient,

$$\mu_T = \left(\frac{\partial H}{\partial p} \right)_T. \quad (5.17)$$

We can find a relation between these two with the permutation rule.

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \quad (5.18)$$

$$= - \left(\frac{\partial T}{\partial H} \right)_p \left(\frac{\partial H}{\partial p} \right)_T \quad (5.19)$$

$$= - \frac{\left(\frac{\partial H}{\partial p} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_p} \quad (5.20)$$

$$= - \frac{\mu_T}{C_p} \quad (5.21)$$

5.2 Exact and inexact differentials

The existence of equations of state means that it is only necessary to specify two of the three variables p, V, T for a system containing a single substance. Therefore, thermodynamic functions for one-component systems can be regarded as functions of only two variables (rather than three), and which two to choose is purely a matter of convenience. Usually U is thought of as a function of T and V and H as a function of T and p ; some formulas take on somewhat simpler forms if those choices are made, but there is nothing magic about them.

If we want to know a change in U during some process, we can write the *total differential* of U as

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (5.22)$$

All sorts of quantities in thermodynamics have total differentials that can be written in that way. Carrying out integrations of such quantities, to find overall changes during some process, usually requires knowing how T and V change while the process is going on (in the language of multivariable calculus, you must be able to carry out a “line integral” in the T, V plane.) For some special differentials, called exact differentials, it does not matter what path in the T, V space is used; the integral is the same in any case. These are the differentials of state functions. How can we tell whether a particular differential is exact or not?

There’s a rule, called the Euler criterion, for deciding whether a particular differential is exact. If you have a differential

$$dz = f(x, y) dx + g(x, y) dy, \quad (5.23)$$

then the differential dz is exact if and only if

$$\left(\frac{\partial f(x, y)}{\partial y} \right)_x = \left(\frac{\partial g(x, y)}{\partial x} \right)_y. \quad (5.24)$$

Here's a trivial example. Consider the internal energy change during an expansion of an ideal gas. We can rewrite Eq. (5.22) as

$$dU = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (5.25)$$

For an ideal gas, $\left(\frac{\partial U}{\partial V} \right)_T = 0$, so

$$dU = C_V dT + 0 dV \quad (5.26)$$

In terms of the form needed for the Euler criterion, we have $x = T$, $y = V$, $f(x, y) = C_V$, and $g(x, y) = 0$. Then the Euler criterion says that dU is exact if and only if

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial 0}{\partial T} \right)_V \quad (5.27)$$

On the left, we have

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V \right)_T \quad (5.28)$$

The order of partial differentiation does not matter if the derivatives are continuous, so

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right)_V \quad (5.29)$$

But we know that $\left(\frac{\partial U}{\partial V} \right)_T = 0$ for an ideal gas. Since both sides are equal to 0, we find that dU is an exact differential (which we knew all along.)

There is an important error in E&R on this point. They claim in Appendix A.6 that the order of partial derivatives is immaterial only for state functions. That's not true; their equation A.60,

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial f(x, y)}{\partial x} \right)_y \right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial f(x, y)}{\partial y} \right)_x \right)_y \quad (\text{E\&R A.60})$$

is the same one I gave above as a general statement for functions with continuous derivatives. It is satisfied by all functions $f(x, y)$ with continuous derivatives, not just state functions. You must use the Euler criterion to determine reliably whether a differential is exact or not, and therefore whether it is the differential of a state function.

5.2.1 Prelude to the Second Law: the quantities dq and dq/T

Let us consider the differential dq for a reversible process in an ideal gas. We have

$$dq = dU - dw = C_V dT + P dV \quad (5.30)$$

For this to be exact, we would have to have

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial C_V}{\partial V}\right)_T. \quad (5.31)$$

For an ideal gas, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$. As above, for an ideal gas, the right hand side is equal to 0. Therefore dq is not an exact differential, because $\frac{nR}{V} \neq 0$.

If we consider, still for the reversible process, $\frac{dq}{T}$, we find

$$\frac{dq}{T} = \frac{C_V}{T} dT + \frac{P}{T} dV \quad (5.32)$$

and the Euler criterion is

$$\left(\frac{\partial(C_V/T)}{\partial V}\right)_T = \left(\frac{\partial(P/T)}{\partial T}\right)_V \quad (5.33)$$

$$\frac{1}{T} \left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial(nR/V)}{\partial T}\right)_V \quad (5.34)$$

$$0 = 0 \quad (5.35)$$

so that dq/T is exact. We have shown this only for reversible processes in ideal gases, but it holds true in general: dq/T is the differential of a state function, called the entropy, for all processes in all substances. The Second Law of thermodynamics, which states what processes can happen without the expenditure of work from the surroundings, is most simply stated in terms of the entropy.

Chapter 6

The Second Law

6.1 Statements of the Second Law

We now come to one of the most interesting topics in all of science. Like all scientific “laws”, the Second Law of thermodynamics is an *abstraction from experience*: it is a succinct statement of a large collection of experimental observations. It is not something that can be “proven”, but is a rule that Nature has appeared to follow any time anyone has looked carefully.

In this section I want to state the second law and show that it implies the existence of a state function that does not change along any reversible adiabatic path. We will name this state function “entropy”; it underlies every discussion of chemical equilibrium. My development in this section follows that given in *Physical Chemistry* by Berry, Rice, and Ross (Wiley, 1980).

Many different but equivalent statements of the Second Law have been given. Let me list a few:

1. (Clausius) It is impossible to devise a continuously cycling engine that produces no effect other than the transfer of heat from a colder to a hotter body.
2. (Kelvin) It is impossible to devise a continuously cycling engine that produces no effect other than the extraction of heat from a reservoir at one temperature and the performance of an equivalent amount of work.
3. (Caratheodory) In the neighborhood of every equilibrium state of a closed system there are states that cannot be reached from the first state along any adiabatic path.

Notice the importance given to *cyclic* processes: those that return the system to its original state. This emphasis arose historically from the study of mechanical engines. An engine is useless unless it is cyclic; if the pistons can only move up and down once in the cylinders before the engine must be thrown away, it isn't much good. A useful engine gets energy from somewhere, converts some of it (but not all of it, as we shall see), to work, the remainder to heat, and *returns to its original state* to start again. The motivation for the work that led up to the Second Law was to find out what controlled how much of the available energy could be converted to work.

It is easy to come up with processes that move heat from a colder to a hotter body. For example, we can put some gas in a cylinder and let it come to thermal equilibrium with an object at temperature T_1 . If we then pull the piston out, so that the gas expands isothermally, as we have seen it will extract heat from the object. Now, we remove the cylinder from the object, isolate it thermally, and compress the gas. Since the cylinder is isolated, the compression is adiabatic, and the gas temperature will rise; by doing enough work on the gas, we can make its temperature rise to temperature T_3 . Now we bring the gas into thermal contact with another object whose temperature is T_2 , such that $T_3 > T_2 > T_1$. Heat will flow from the gas into the second body. We have now moved heat from the first object to the second, even though the second was at a higher temperature. However, the gas in the cylinder is no longer in the same state it was before; its volume is smaller, and its temperature higher, than at the beginning. This process does not violate the Second Law.

6.2 Existence of the entropy

Figure 6.1 shows the T, V diagram for a one-component, closed system. The path from point 1 to point 2 is a reversible, adiabatic path. The path from point 2 to point 3 is a reversible, isothermal path. I now ask the question: can we find any reversible, adiabatic path from point 3 back to point 1?

Let me assume we can. We know, because the system returns to point 1, that $\Delta U = 0$ for the whole cycle. Therefore, $w = -q$ for the whole cycle.

The path $1 \rightarrow 2$ is a reversible adiabat; adiabatic means $q_{1 \rightarrow 2} = 0$. The path $2 \rightarrow 3$ is a reversible isothermal expansion; such an expansion requires $q_{2 \rightarrow 3} > 0$. Finally, the path $3 \rightarrow 1$ is a reversible adiabat with $q_{3 \rightarrow 1} = 0$. Therefore, overall, $q > 0$, and since $q = -w$, we have $w < 0$. This cycle therefore converts heat drawn from a reservoir at temperature T_2 (the temperature of points 2 and 3, and the temperature of the only section of the cycle where any heat is transferred) into an equivalent amount of work. It therefore violates Kelvin's statement of the Second

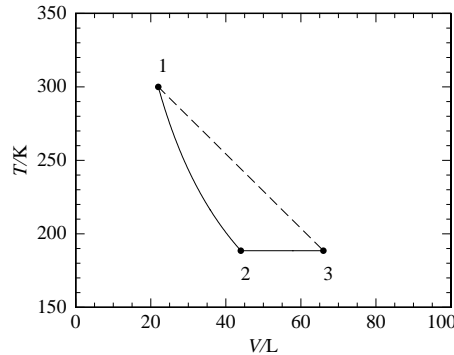


Figure 6.1: A cycle in the T, V plane. Section $1 \rightarrow 2$ is a reversible adiabat; section $2 \rightarrow 3$ is a reversible isotherm.

Law. There is no reversible adiabat connecting points 1 and 3.

This argument holds for any substance and any isothermal path $2 \rightarrow 3$, so we find that through point 1 *there is only one reversible adiabatic path*. In other words, reversible adiabats cannot cross on a T, V diagram.

Because the reversible adiabats cannot cross, we can describe any reversible adiabatic curve with a function $T(V)$, or equivalently, $f(T, V) = \text{constant}$. Let me name such a function $S(T, V)$; I will call it the entropy, and it will be constant along any reversible adiabatic curve. Therefore $dS(T, V) = 0$ along any reversible adiabat through (T, V) .

I have not given any detailed formula for $S(T, V)$ yet; I still need to find a formula. But the existence of such a function is guaranteed by the uniqueness of the reversible adiabats.

We already saw, in the Mathematical Interlude section, that the differential dq/T was exact for a reversible process, that is, was the differential of a state function. Since the entropy is constant along any reversible adiabatic path, changes in entropy in a reversible system must involve a nonzero heat flow. Those observations lead to an acceptable formula for changes in the entropy:

$$dS = \frac{dq_{\text{rev}}}{T}. \quad (6.1)$$

For any change,

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}. \quad (6.2)$$

This formula lets us compute changes in entropy, but does not give an absolute value for S for a particular system. Statistical mechanics, and the Third Law of

thermodynamics, do allow for the assignment of absolute entropy values; we will encounter those shortly. Nonetheless, for S as well as for H and U , it's the changes that will concern us most.

The formula for dS involves the heat transfer in a *reversible* process. If the process you are interested in is (like most processes) not reversible, then to calculate ΔS you must find some reversible path that gets you from the same initial to the same final state, evaluate ΔS for each leg of that path, and add them all together. Since S is a state function, that gives you the correct answer even though the real path is not reversible.

6.3 Examples of entropy calculations

The following examples are typical of entropy calculations for reversible processes; you must figure out an expression for dq_{rev} , then integrate it over the process. For irreversible processes, you must identify some reversible path that takes your system between the same initial and final states.

Remember that a simple symbol like ΔS refers to the *system*; we will see shortly how to calculate entropy changes in the surroundings.

6.3.1 Reversible isothermal processes

In an isothermal change, T is constant. If the change is reversible, or (since S is a state function) can be replaced by a reversible change with the same initial and final states, then we have simply

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}. \quad (6.3)$$

Reversible isothermal expansion of ideal gas For reversible isothermal expansion of an ideal gas we have $\Delta U = 0$ so $q_{\text{rev}} = -w = nRT \ln(V_2/V_1)$. So

$$\Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \left(\frac{V_2}{V_1} \right). \quad (6.4)$$

Notice that the entropy change is positive for an expansion, negative for a compression.

Phase changes in pure substances Phase changes — melting, boiling, sublimation, and transitions from one crystalline phase to another — generally occur at constant temperature. We can bring them about reversibly in a very natural way,

by making sure the source of heat is held very nearly at the transition temperature (for example, at the melting point.) If the phase change occurs at constant pressure, then we have $q_{\text{rev}} = \Delta H$, so that

$$\Delta_{\text{trs}}S = \frac{q_{\text{rev}}}{T} = \frac{\Delta_{\text{trs}}H}{T_{\text{trs}}}, \quad (6.5)$$

where T_{trs} is the transition temperature. So, for example, the molar entropy change for melting of ice at 1 bar is

$$\Delta_{\text{fus}}S^\ominus = \frac{\Delta_{\text{fus}}H^\ominus}{T_{\text{fus}}} = \frac{6.01 \text{ kJ/mol}}{273.15 \text{ K}} = 22.0 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (6.6)$$

6.3.2 Reversible heating or cooling at constant P

To heat or cool something reversibly, you bring it in contact with another object (the “reservoir” or “bath”) whose temperature is almost exactly equal to your object. In this case, the direction of heat flow could be reversed by changing the temperature of the object infinitesimally, so the heat flow is reversible. As your object warms or cools, you must adjust the temperature of the bath so that it “tracks” your object. Then $dq_{\text{rev}} = C_p dT$, and

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT. \quad (6.7)$$

If C_p is constant over the temperature range of interest we find

$$\Delta S = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right). \quad (6.8)$$

6.3.3 Irreversible heat transfer

Say 100 g of water at 80 °C is mixed in a Dewar flask with 100 g of water at 20 °C. You can show that the final temperature will be 50 °C. What is the total entropy change?

This mixing is irreversible; the two temperatures are not the same when the samples come into contact, so an infinitesimal change in the temperature of one sample will not reverse the direction of the heat transfer. To find the overall entropy change, we must find a reversible path between the two states.

A simple reversible path is this:

1. Cool sample A reversibly from 80 to 50 °C.
2. Heat sample B reversibly from 20 to 50 °C.

3. Add the two samples together; no heat flows in this process, so $\Delta S = 0$.

We must calculate the entropy changes for the heating of sample A and the cooling of sample B, and add them together.

For the heating process, we have

$$dS = \frac{dq_{\text{rev}}}{T} = C_p \frac{dT}{T} \quad (6.9)$$

$$\Delta S_A = \int_{T_A}^{T_f} C_p \frac{dT}{T} \quad (6.10)$$

$$= C_p \ln\left(\frac{T_f}{T_A}\right) \quad (6.11)$$

Similarly, for sample B we find

$$\Delta S_B = C_p \ln\left(\frac{T_f}{T_B}\right) \quad (6.12)$$

so the total entropy change in the sample is

$$\Delta S = C_p \left[\ln\left(\frac{T_f}{T_A}\right) + \ln\left(\frac{T_f}{T_B}\right) \right]. \quad (6.13)$$

Since the heating and cooling steps were carried out reversibly, the change in entropy in the surroundings (which supplied the heat to warm sample B, and received the heat from the cooling of sample A) were exactly opposite those in the samples, so the overall change in entropy of the universe for this reversible path is zero. That is another possible definition of “reversible”.

6.3.4 Entropy changes in the surroundings

If we can regard the surroundings of any thermodynamic process as existing at constant temperature and pressure, then

$$dH_{\text{surr}} = dq_{\text{surr}}, \quad (6.14)$$

and since the enthalpy is a state function, changes in it are independent of whether the heat transfer occurs reversibly or not; therefore, when the surroundings are at constant T and P ,

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T}. \quad (6.15)$$

Similarly, if the surroundings are at constant T and V , then

$$\Delta S_{\text{surr}} = \frac{\Delta U_{\text{surr}}}{T}. \quad (6.16)$$

So under those conditions it is easy to calculate entropy changes in the surroundings. This idea is extremely powerful in considerations of chemical equilibrium, and is the motivation for the introduction of the familiar Gibbs and Helmholtz energies.

6.3.5 Irreversible processes: the Clausius inequality

Consider again our water-mixing problem. We found that for the sample,

$$\Delta S = C_p \left[\ln \left(\frac{T_f}{T_A} \right) + \ln \left(\frac{T_f}{T_B} \right) \right], \quad (6.17)$$

while along the reversible path the entropy changes in the surroundings exactly cancelled those of the system so that the total entropy change was zero. What about along the original, irreversible path? If we just dump both samples into a Dewar flask together, then no heat flows into the surroundings, so the entropy change in the surroundings is zero. The entropy change in the system is the same as before (entropy is a state function.) Examine the sign of the entropy change in the system:

$$\Delta S = C_p \left[\ln \left(\frac{T_f}{T_A} \right) + \ln \left(\frac{T_f}{T_B} \right) \right] \quad (6.18)$$

$$= C_p \left[\ln \left(\frac{T_f T_f}{T_A T_B} \right) \right] \quad (6.19)$$

$$(6.20)$$

The entropy change in the system will be positive if the argument of the logarithm is greater than 1. Examine that argument:

$$\frac{T_f T_f}{T_A T_B} = \frac{\left(\frac{T_A + T_B}{2} \right)^2}{T_A T_B} \quad (6.21)$$

$$= \frac{T_A^2 + 2T_A T_B + T_B^2}{4T_A T_B} \quad (6.22)$$

$$= \frac{1}{2} + \frac{T_A^2 + T_B^2}{4T_A T_B} \quad (6.23)$$

$$= \frac{1}{2} + \frac{1}{4} \left(\frac{T_A}{T_B} + \frac{T_B}{T_A} \right) \quad (6.24)$$

Under what conditions will that argument be greater than 1? We need

$$\frac{1}{2} + \frac{1}{4} \left(\frac{T_A}{T_B} + \frac{T_B}{T_A} \right) > 1 \quad (6.25)$$

$$\frac{T_A}{T_B} + \frac{T_B}{T_A} > 2 \quad (6.26)$$

$$\left(\frac{T_A}{T_B} \right)^2 + 1 > 2 \frac{T_A}{T_B} \quad (6.27)$$

$$\left(\frac{T_A}{T_B} - 1 \right)^2 > 0 \quad (6.28)$$

which will be true for any $T_A \neq T_B$. In other words, the entropy change of this isolated system is greater than zero for the irreversible process. That is true in general, not just for irreversible heat transfers, and is known as the *inequality of Clausius*: for any spontaneous process in an isolated system, $\Delta S > 0$. That inequality will drive all the rest of our discussions of equilibrium.

Chapter 7

Gibbs and Helmholtz energies

7.1 Total entropy changes

In any isolated system, for any spontaneous (that is, natural) process, $\Delta S > 0$. It is useful to regard the entire universe—system plus surroundings—as an isolated system. This outlook lets us, as Atkins puts it, “concentrate on the system” while making reliable predictions about what processes will be spontaneous.

If we divide the universe into system and surroundings (or at least that part of the surroundings that interacts with the system) then we must have, for any small spontaneous change,

$$dS + dS_{\text{surr}} > 0. \quad (7.1)$$

(Keep in mind that unsubscripted quantities refer to the *system*.) If the system is at constant temperature and pressure, then the heat that flows into the surroundings is $-dq_p = -dH$, where dH is the enthalpy change in the system. The entropy change in the surroundings is, since the surroundings may be assumed isothermal,

$$dS_{\text{surr}} = -\frac{dH}{T} \quad (7.2)$$

leading to

$$dS - \frac{dH}{T} > 0. \quad (7.3)$$

If we multiply both sides by $-T$, (a negative quantity, so we must reverse the inequality), we find

$$dH - T dS < 0. \quad (7.4)$$

We have found a requirement on changes in state functions of the *system* that specifies whether a process is spontaneous or not on the basis of entropy changes

in the universe, under the assumption that the system (and universe) are at constant temperature and pressure.

An analogous argument, for the case of a system at constant temperature and volume, is the same except that the heat flow into the surroundings is given by $-dq_V = -dU$. Following the argument exactly as before gives us the criterion for spontaneous processes at constant temperature and volume

$$dU - TdS < 0. \quad (7.5)$$

Those two inequalities, which are criteria for spontaneous change in systems at constant pressure or constant volume, suggest the definitions of two new state functions:

$$G = H - TS \quad (7.6)$$

$$A = U - TS \quad (7.7)$$

These are called the Gibbs and Helmholtz energies (or “free energies”). With them the spontaneity criteria become

$$dG < 0 \quad (7.8)$$

$$dA < 0 \quad (7.9)$$

Often you will hear a statement something like “There is a tradeoff between changes in energy and entropy; systems want to be at low energy and high entropy, and whichever one “wins” determines the direction of spontaneous change.” That statement, while operationally workable, misses the fundamental point. The direction of spontaneous change is determined *entirely* by changes in overall entropy of the universe. Under conditions of constant temperature and pressure, the Gibbs function will decrease if a system undergoes a change that increases the universe’s entropy. That is why the Gibbs function is useful. A large negative ΔH indicates that the reaction will dump a lot of heat into the surroundings, increasing the entropy of the surroundings; that helps increase the entropy of the universe, and can compensate for decreases of the system’s entropy. Similarly, if the system is at constant T and V , its Helmholtz function will decrease if the entropy of the universe increases. Both are useful because they let you predict entropy changes in the universe on the basis of more-easily-calculable changes in the system itself.

7.1.1 Aside: reversibility and maxima

From the Clausius inequality we can draw some conclusions that will be useful shortly. You know that for any change in the system, $dS = \frac{dq_{\text{rev}}}{T}$, and you know that

$dS + dS_{\text{surr}} \geq 0$ (where the equality holds only for reversible processes). We already saw that entropy changes in the surroundings at constant T do not depend on whether the process is carried out reversibly or irreversibly, so $dS_{\text{surr}} = \frac{-dq}{T}$. Then we have

$$\frac{dq_{\text{rev}}}{T} + \frac{-dq}{T} \geq 0, \quad (7.10)$$

whence

$$dq_{\text{rev}} \geq dq, \quad (7.11)$$

or

$$dS \geq \frac{dq}{T}, \quad (7.12)$$

where all variables without subscripts apply to the system. In fact, Eq. (7.12) is sometimes called the Clausius inequality.

Straightforward arguments (outlined in your text) can show that ΔA for a process gives the maximum amount of work that can be extracted from an isothermal process, and ΔG for a process gives the maximum amount of non-expansion work that can be extracted from the process. I will not prove those things; after a brief demonstration that the maximum work is obtained when a process acts reversibly, we will go on toward relations that apply to reacting systems.

7.2 Alphabet soup: Maxwell relations and thermodynamic equations of state

We now begin finding formulas that we can use to make predictions about chemistry.

The First Law gives

$$dU = dq + dw. \quad (7.13)$$

Restrict the discussion to reversible (equilibrium) processes doing only expansion (PV) work. Then $dq = dq_{\text{rev}} = T dS$ and $dw = -P dV$ so we have

$$dU = T dS - P dV. \quad (7.14)$$

dU is an exact differential. We could have regarded U as a function of S and V and written immediately

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV. \quad (7.15)$$

Comparing Eq. (7.14) and Eq. (7.15) gives

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (7.16)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad (7.17)$$

Also, because dU is an exact differential, the Euler criterion holds so that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_T \quad (7.18)$$

Eq. (7.18) is one of four *Maxwell relations* that provide routes between things one is interested in (like, how the internal energy changes with volume) and things one can measure (like heat capacities, changes of temperature with pressure, and so on.) The other three are derived in exactly the same way, by applying the Euler criterion to the differentials of H , G , and A . In Table 7.1 I list the results; you should be able to derive any expression in the later columns from the equation in the first.

Table 7.1 The Gibbs equations (first column), the resulting thermodynamic identities (second and third), and the corresponding Maxwell relations (last column).

$dU = T dS - P dV$	$\left(\frac{\partial U}{\partial S}\right)_V = T$	$\left(\frac{\partial U}{\partial V}\right)_S = -P$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
$dH = T dS + V dP$	$\left(\frac{\partial H}{\partial S}\right)_P = T$	$\left(\frac{\partial H}{\partial P}\right)_S = V$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$dA = -S dT - P dV$	$\left(\frac{\partial A}{\partial T}\right)_V = -S$	$\left(\frac{\partial A}{\partial V}\right)_T = -P$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
$dG = -S dT + V dP$	$\left(\frac{\partial G}{\partial T}\right)_P = -S$	$\left(\frac{\partial G}{\partial P}\right)_T = V$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

7.2.1 Application: internal pressure of a van der Waals gas

That ferocious-looking table can be used to answer real questions. The first I will show is one that you did part of in your homework: show that $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$ for a van der Waals gas.

The trick is to change things you don't know how to evaluate into things you do by looking for substitutions. Here we go:

7.2. Alphabet soup: Maxwell relations and thermodynamic equations of state 95

We don't have $\left(\frac{\partial U}{\partial V}\right)_T$ in our table anywhere. But we do have $\left(\frac{\partial U}{\partial V}\right)_S$. Recall that we have a formula that lets you change the subscript on a partial derivative, by adding a fixup term. Looking up that formula (several pages back) gets us

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T. \quad (7.19)$$

In our table, we find simple expressions for two of those things:

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad (7.20)$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (7.21)$$

giving

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \left(\frac{\partial S}{\partial V}\right)_T. \quad (7.22)$$

The remaining partial derivative has an S in it, which does not appear in our van der Waals equation of state, but there is a substitution for it in the table, giving us

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V. \quad (7.23)$$

So far nothing we have done has made any approximations or assumed any properties of a particular substance. Now we assume that the substance is a van der Waals gas, and we can evaluate that last term directly from the van der Waals equation. We have

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (7.24)$$

so that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m - b} \quad (7.25)$$

Substituting that into Eq. (7.23) gives

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + \frac{RT}{V_m - b} = \frac{a}{V_m^2} \quad (7.26)$$

after a simple substitution from the van der Waals equation.

7.3 The chemical potential

The Gibbs equations and their associated formulas we saw in the last section hold for closed systems undergoing only reversible processes (possibly including reversible changes in composition, but not ordinary irreversible chemical reactions beginning far from equilibrium). To make thermodynamics useful in chemistry we need to extend it to account for open systems and irreversible composition changes. We can therefore no longer regard our state functions G , S , and so on as functions of two variables only, but must add additional variables to account for composition changes. In chemistry, the Gibbs energy is the most valuable energy function, so I will concentrate on its dependence on composition.

We had, for systems at mechanical, thermal, and material (reaction) equilibrium, with only PV work possible,

$$dG = -S dT + V dP \quad (7.27)$$

That equation is a friendlier-looking version of

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP. \quad (7.28)$$

To account for addition of material (by reaction or simple addition), we just add terms. If we want to evaluate a small change in G when the pressure, temperature, or number of moles of substance k changes, we write

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_k} dP + \left(\frac{\partial G}{\partial n_k}\right)_{T,P} dn_k \quad (7.29)$$

If we have many different components, with numbers of moles of each one written as n_i , $i = 1, 2, 3 \dots k$, then we write

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_{i \neq 1}} dn_1 \\ + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_{i \neq 2}} dn_2 + \dots + \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_{i \neq k}} dn_k \quad (7.30)$$

which I can write as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^k \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}} dn_i \quad (7.31)$$

We define the *chemical potential* of species i in a one-phase system (not necessarily a pure material: this holds for different chemical species in a solution, for example) as

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}} \quad (7.32)$$

The chemical potential tells how the Gibbs energy of a system changes when a substance is added to it. It is an *intensive* quantity since it is the ratio of two extensive quantities (G and n).

Our Gibbs equation now returns to a friendlier-looking form:

$$dG = -S dT + V dP + \sum_{i=1}^k \mu_i dn_i \quad (7.33)$$

According to Levine: “(Eq. (7.33)) is the key equation in chemical thermodynamics.” It applies to a single-phase system, internally at thermal and mechanical (but not chemical) equilibrium, where only PV work is considered.

If you go through all the thermodynamic energy functions U , H , A , and G , you will find by simple substitutions that their Gibbs equations are all extended to the variable-composition case by adding a term

$$+ \sum_{i=1}^k \mu_i dn_i$$

to them. The same chemical potentials can be used for all four.

As an example, let me find the new, variable-composition total differential for the internal energy U . We have $G = H - TS = U + PV - TS$, so $U = G - PV + TS$. Then taking the total differential gives

$$dU = dG - PdV - VdP + TdS + SdT \quad (7.34)$$

$$= -SdT + VdP + \sum_{i=1}^k \mu_i dn_i - PdV - VdP + TdS + SdT \quad (7.35)$$

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i, \quad (7.36)$$

and you can see that this result is just the old one ($dU = TdS - PdV$) with an added term for composition changes that is the same one we added to dG .

The new Gibbs equations, with chemical potential terms added, apply to single-phase systems, either open or closed, in mechanical and thermal equilibrium. (“Mechanical and thermal equilibrium” implies that P and T are uniform throughout the phase.) They are applicable to systems undergoing chemical reactions far from equilibrium and also to systems to which material is being added or removed. The expressions do not yet apply to multi-phase systems, though as we will see shortly the extension to multiple phases is straightforward.

7.3.1 Chemical potential of a pure substance

If there is only one component, then we have

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,P} = \left(\frac{\partial n G_m}{\partial n} \right)_{T,P} = G_m, \quad (7.37)$$

since the molar Gibbs energy G_m is an intensive quantity independent of n . Therefore for a pure substance the chemical potential is simply the molar Gibbs energy.

Variation of chemical potential with pressure of ideal gas

We have for a one-component system in equilibrium

$$dG = -S dT + V dP$$

If we consider an isothermal change of pressure of an ideal gas, we find

$$\Delta G = \int_{P_1}^{P_2} V dP \quad (7.38)$$

$$= \int_{P_1}^{P_2} \frac{nRT}{P} dP \quad (7.39)$$

$$= nRT \ln \left(\frac{P_2}{P_1} \right) \quad (7.40)$$

Now if we define one particular pressure (nowadays usually one bar) as the “standard pressure”, then we can say

$$G(P) = G^\ominus + nRT \ln \left(\frac{P}{P^\ominus} \right) \quad (7.41)$$

Differentiating with respect to n , we find (since for a pure substance $\mu = G_m = G/n$)

$$\mu(P) = \mu^\ominus + RT \ln \left(\frac{P}{P^\ominus} \right) \quad (7.42)$$

This tells us, for a pure perfect gas, how the chemical potential varies with pressure.

7.3.2 Multiple phases

In many problems more than one phase is present. For example, in the preparation of a Grignard reagent the organohalogen compound is typically present

in solution, in contact with solid Mg. In the melting of ice both solid and liquid water are present, and so on. It is easy to extend Eq. (7.33) to multiple phases; in addition to a sum over the different substances present, we also need a sum over the phases. Each substance has a chemical potential for each phase (that is, the chemical potential of a given substance might be different in different phases.) We write, for k substances in m phases,

$$dG = -S dT + V dP + \sum_{\alpha=1}^m \sum_{i=1}^k \mu_i^\alpha dn_i^\alpha \quad (7.43)$$

where the superscript α denotes the phase. In Eq. (7.43), S and V refer to the *total* entropy and volume of the system (the sums of those quantities for all phases).

7.4 Conditions for material equilibrium

At the beginning of this chapter we saw that the criterion for spontaneous (that is, natural, or possible) change at constant T and P is downhill in G , that is, $dG < 0$. At equilibrium, then, when neither direction is downhill, we expect $dG = 0$; at constant T and P , Eq. (7.43) then reads

$$\sum_{\alpha=1}^m \sum_{i=1}^k \mu_i^\alpha dn_i^\alpha = 0. \quad (7.44)$$

If we consider a system at constant T and V , then the equilibrium condition is $dA = 0$; because the chemical potential terms are the same for dA as for dG , the condition for equilibrium is still given by Eq. (7.44). In fact, Eq. (7.44) is a general condition for material equilibrium; it is true for any closed system in material equilibrium, not matter what the conditions are. If the system is at constant T and P , Eq. (7.44) corresponds to $dG = 0$; if it is at constant T and V , it corresponds to $dA = 0$; under other conditions it corresponds to neither, but it still is the requirement for material equilibrium to be achieved.

In general, material will “flow” from a phase with high chemical potential to one with low chemical potential. The “flow” may correspond to a chemical reaction or to a phase change (evaporation, dissolving, etc.) At equilibrium, there is no change in composition that is “downhill”; changing a tiny amount of A into a tiny amount of B generates no net decrease in the overall chemical potential.

Chemical potentials are intensive, like T and P , and they depend on the concentrations of all the substances present in a phase. We have not proved it, but the chemical potential of a substance in a particular phase always increases if the mole fraction of that substance is increased by simple addition of more of it at

constant T and P (see Levine, 6th edition, section 4.7 for references.) So stuffing more and more of a substance into a particular phase becomes harder and harder. Some authors refer to the chemical potential as a measure of “escaping tendency”; the higher the chemical potential, the more a substance wants to leave a given phase (by transfer to another phase or by reaction) and go somewhere else.

7.4.1 Phase equilibrium

Consider the simplest sort of phase equilibrium, the partitioning of a single pure substance between two phases (for instance, the evaporation of water in a closed flask). Eq. (7.44) says that at equilibrium, the sum

$$\mu_l dn_l + \mu_g dn_g = 0, \quad (7.45)$$

where the subscript l indicates liquid and g indicates gas. Because the system is closed, and only the two phases are present, we must have $dn_l = -dn_g$. Substituting for dn_l and rearranging I find

$$(\mu_g - \mu_l) dn_g = 0 \quad (7.46)$$

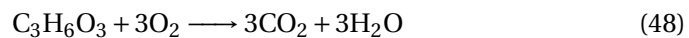
or, dividing by dn_g ,

$$\mu_g = \mu_l. \quad (7.47)$$

In other words, equilibrium is reached when the chemical potentials of the water in the liquid and the gas are equal. That is the general case: in a closed system, at material equilibrium every substance has the same chemical potential in all the phases in which it appears.

7.4.2 Reaction equilibrium

When a chemical reaction occurs in a closed system, the change dn_A in the number of moles of A is proportional to its stoichiometric coefficient ν_A in the balanced chemical equation (ν_A is positive if A is a product, negative if it is a reactant). The proportionality constant, commonly called the “extent of reaction”, is often written ξ . For instance, in the reaction



if $\xi = 0.1$ mol then 0.1 mol of $\text{C}_3\text{H}_6\text{O}_3$ and 0.3 mol of oxygen have been consumed and 0.3 mol each of carbon dioxide and water have been produced.

In a closed system at equilibrium, we just saw that the chemical potential of any species is the same in any phase in which it appears. Therefore, we can

simplify our study of reaction equilibrium by assuming phase equilibrium also holds. Then we have

$$0 = \sum_{\alpha=1}^m \sum_{i=1}^k \mu_i^{\alpha} dn_i^{\alpha} \quad (7.49)$$

$$= \sum_{i=1}^k \sum_{\alpha=1}^m \mu_i^{\alpha} dn_i^{\alpha} \quad (7.50)$$

Since the chemical potential of substance i is the same in all phases α , I can drop the superscript on μ_i and move it through the sum over phases:

$$0 = \sum_{i=1}^k \mu_i \sum_{\alpha=1}^m dn_i^{\alpha} \quad (7.51)$$

$$= \sum_{i=1}^k \mu_i dn_i \quad (7.52)$$

where the last line follows because the sum of the changes in the amount of substance i in all phases is just the total change in the amount of that substance.

Now we consider the change in numbers of moles of each substance brought about by a small increase in the extent of reaction $d\xi$. For each substance we have $dn_i = \nu_i d\xi$. Then the equilibrium condition becomes

$$0 = d\xi \sum_{i=1}^k \mu_i \nu_i \quad (7.53)$$

or, dividing by $d\xi$,

$$\sum_{i=1}^k \mu_i \nu_i = 0. \quad (7.54)$$

This is the general condition for chemical equilibrium in a closed system.

So far I have given several “rules of equilibrium”, which can be written compactly in terms of chemical potentials. They are not useful, though, unless we can find ways to calculate the chemical potentials or to convert the rules into equations relating more easily measurable quantities. I want next to examine chemical equilibria in ideal gas mixtures, giving a concrete example of the power of the chemical potential idea.

7.5 Reaction equilibrium in ideal gases

We saw earlier that for a pure ideal gas at pressure P , the chemical potential $\mu = \mu^{\circ} + RT \ln(P/P^{\circ})$, where μ° is the chemical potential at pressure P° . For an

ideal gas mixture, we regard each mixture component as independent, so that the same equation holds, but with P interpreted as the partial pressure of each gas. Then

$$\mu_i(T) = \mu_i^\circ(T) + RT \ln\left(\frac{P_i}{P^\circ}\right) \quad (7.55)$$

The equilibrium condition, Eq. (7.54), becomes

$$\sum_{i=1}^k \nu_i \left[\mu_i^\circ(T) + RT \ln\left(\frac{P_i}{P^\circ}\right) \right] = 0 \quad (7.56)$$

Collecting the standard-state chemical potentials on the left, I have

$$\sum_{i=1}^k \nu_i \mu_i^\circ(T) = -RT \sum_{i=1}^k \nu_i \ln\left(\frac{P_i}{P^\circ}\right) \quad (7.57)$$

In an ideal gas mixture, where there are no interactions between the different gas species, the individual gases act as though they were pure. Therefore, the chemical potentials on the left side are the chemical potentials of the pure gases, that is, they are the molar Gibbs energies of the different gases. The sum on the left side is therefore the standard molar Gibbs energy of the reaction:

$$\sum_{i=1}^k \nu_i \mu_i^\circ(T) = \sum_{i=1}^k \nu_i G_{i,m}^\circ(T) = \Delta_r G_T^\circ \quad (7.58)$$

Now we have

$$\Delta_r G_T^\circ = -RT \sum_{i=1}^k \nu_i \ln\left(\frac{P_i}{P^\circ}\right) \quad (7.59)$$

A multiplier in front of a logarithm becomes an exponent inside the logarithm, and a sum of logs is the log of a product, so this is

$$\Delta_r G_T^\circ = -RT \ln \prod_{i=1}^k \left(\frac{P_i}{P^\circ}\right)^{\nu_i} \quad (7.60)$$

This is a very familiar equation, though you might not recognize it yet! Take, as an example, the ideal gas reaction



Now $\nu_a = -a$, $\nu_c = c$, and so on, and we have

$$\Delta_r G_T^\circ = -RT \ln \left(\frac{(P_C/P^\circ)^c (P_D/P^\circ)^d}{(P_A/P^\circ)^a (P_B/P^\circ)^b} \right). \quad (7.62)$$

You should recognize the standard pressure equilibrium constant,

$$K_P^\ominus = \left(\frac{(P_C/P^\ominus)^c (P_D/P^\ominus)^d}{(P_A/P^\ominus)^a (P_B/P^\ominus)^b} \right), \quad (7.63)$$

where all the species pressures are equilibrium values. In the more general notation,

$$K_P^\ominus = \prod_{i=1}^k \left(\frac{P_i}{P^\ominus} \right)^{\nu_i} \quad (7.64)$$

Our equilibrium condition is now

$$\Delta_r G_T^\ominus = -RT \ln K_P^\ominus(T) \quad (7.65)$$

and we have derived the existence of a standard equilibrium constant that depends only on T .

7.6 Phase equilibrium: the Clapeyron equation

I want to use the chemical potential idea to determine the behavior of phase equilibrium in a two-phase system. Imagine that we have water and ice in equilibrium at 0°C and 1 bar. If we change the temperature without changing the pressure, either the ice will melt (if we raise the temperature) or the water will freeze (if we lower it). Similarly, if we change the pressure without changing the temperature, either the ice will melt (if we raise the pressure, since ice occupies more volume than water) or the water will freeze (if we lower the pressure). But, it's possible to change both the pressure and the temperature simultaneously and maintain both liquid and solid phases in equilibrium. It's the relation between P and T along that "equilibrium line" that is the topic of this discussion.

You should recall the elementary P - T "phase diagram" from freshman chemistry; an example is shown in Figure 7.1. Each curve on the phase diagram shows a function $P(T)$ along which two phases can coexist in equilibrium; at any other point on the diagram, only one phase can be present.

Figure 7.1: Phase diagram for water.

Our general condition for material equilibrium, applied to any point where two phases α and β coexist, is

$$\mu^\alpha(T, P) = \mu^\beta(T, P) \quad (7.66)$$

or, taking the total differential of both sides so that we can study what happens when a small amount of one phase changes into the other,

$$d\mu^\alpha(T, P) = d\mu^\beta(T, P). \quad (7.67)$$

Writing out the total differentials gives

$$\left(\frac{\partial\mu^\alpha}{\partial T}\right)_P dT + \left(\frac{\partial\mu^\alpha}{\partial P}\right)_T dP = \left(\frac{\partial\mu^\beta}{\partial T}\right)_P dT + \left(\frac{\partial\mu^\beta}{\partial P}\right)_T dP \quad (7.68)$$

Recall that for a pure substance (that is, either phase in our case) the chemical potential is just the molar Gibbs energy:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P}, \quad (7.69)$$

so that the partial derivatives of μ are “mixed second partial derivatives”, the derivative of G with respect to both n and either P or T . In such a mixed derivative, the order of differentiation is unimportant, so we can switch the order and do the differentiation with respect to T or P first. Then we have

$$\frac{\partial}{\partial n_\alpha} \left(\frac{\partial G_\alpha}{\partial T}\right)_P dT + \frac{\partial}{\partial n_\alpha} \left(\frac{\partial G_\alpha}{\partial P}\right)_T dP = \frac{\partial}{\partial n_\beta} \left(\frac{\partial G_\beta}{\partial T}\right)_P dT + \frac{\partial}{\partial n_\beta} \left(\frac{\partial G_\beta}{\partial P}\right)_T dP \quad (7.70)$$

Now, from our thermodynamic relations table, we find the expressions $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$ to give us

$$-\frac{\partial}{\partial n_\alpha} S_\alpha dT + \frac{\partial}{\partial n_\alpha} V_\alpha dP = \frac{\partial}{\partial n_\beta} S_\beta dT + \frac{\partial}{\partial n_\beta} V_\beta dP \quad (7.71)$$

and those derivatives with respect to n just give us the molar entropy and molar volume:

$$-S_{m\alpha} dT + V_{m\alpha} dP = -S_{m\beta} dT + V_{m\beta} dP \quad (7.72)$$

or

$$(V_{m\beta} - V_{m\alpha}) dP = (S_{m\beta} - S_{m\alpha}) dT. \quad (7.73)$$

Now we can get an expression for dP/dT , the slope of the line on the phase diagram, directly:

$$\frac{dP}{dT} = \frac{(S_{m\beta} - S_{m\alpha})}{(V_{m\beta} - V_{m\alpha})} \quad (7.74)$$

$$= \Delta_{\text{trs}} S / \Delta_{\text{trs}} V. \quad (7.75)$$

We are considering the conversion from one phase to another, where the pressures in the two phases are equal. Therefore $\Delta_{\text{trs}} S = \Delta_{\text{trs}} H / T$, giving us

$$\frac{dP}{dT} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V}. \quad (7.76)$$

This equation, exact for any equilibrium phase transition, is the Clapeyron equation. It gives the relation between the equilibrium pressure and temperature of a one-component, two-phase system. It is applicable to all kinds of phase transitions: melting, vaporization, sublimation, and transitions from one solid phase to another.

7.6.1 Phase equilibrium involving an ideal gas

In transitions from condensed phases to gas, if the pressure is far below the critical pressure (where the densities of liquid and gas are the same), the volume of the gas is much larger than the volume of liquid. For example, at ordinary conditions, a mole of water vapor occupies about 25 L while a mole of liquid occupies about 0.018 L, more than a thousand times less. It's therefore a good approximation to replace $\Delta_{\text{trs}} V = V_{\text{gas}} - V_{\text{liq}}$ with simply V_{gas} . If in addition we assume the gas is ideal, so that $V_{\text{gas}} = nRT/P$, then we obtain the *Clausius-Clapeyron equation*

$$\frac{dP}{dT} = \frac{P \Delta_{\text{trs}} H}{nRT^2} \quad (7.77)$$

$$\frac{1}{P} \frac{dP}{dT} = \frac{\Delta_{\text{trs,m}} H}{RT^2} \quad (7.78)$$

$$\frac{d \ln P}{dT} = \frac{\Delta_{\text{trs,m}} H}{RT^2} \quad (7.79)$$

This expression, useful for both vaporization and sublimation, is widely used to predict changes of boiling points with pressure and vapor pressures with temperature.

7.7 Reaction equilibrium: the van't Hoff equation

We have (Eq. (7.65))

$$\Delta_r G_T^\circ = -RT \ln K_p^\circ(T) \quad (7.80)$$

so that

$$\ln K_p^\circ(T) = -\frac{\Delta_r G_T^\circ}{RT} \quad (7.81)$$

Differentiate both sides with respect to T , with P constant:

$$\left(\frac{\partial \ln K_p^\circ(T)}{\partial T}\right)_P = -\frac{1}{R} \left(\frac{1}{T} \left(\frac{\partial \Delta_r G_T^\circ}{\partial T}\right)_P - \frac{\Delta_r G_T^\circ}{T^2}\right) \quad (7.82)$$

Use $\left(\frac{\partial G}{\partial T}\right)_P = -S$:

$$= \frac{1}{R} \left(\frac{1}{T} \Delta_r S_T^\circ + \frac{\Delta_r G_T^\circ}{T^2}\right) \quad (7.83)$$

Now multiply numerator and denominator of the entropy term by T , and recognize $G + TS = H$:

$$= \frac{1}{R} \left(\frac{1}{T^2} T \Delta_r S_T^\circ + \frac{\Delta_r G_T^\circ}{T^2}\right) \quad (7.84)$$

$$= \frac{\Delta_r H_T^\circ}{RT^2} \quad (7.85)$$

Since $K_p^\circ(T)$ is a function of T only, the partial derivative is the same as a total derivative, and we have the van't Hoff equation

$$\frac{d(\ln K_p^\circ(T))}{dT} = \frac{\Delta_r H_T^\circ}{RT^2} \quad (7.86)$$

This equation describes the temperature dependence of equilibrium constants. If you know $\Delta_r H^\circ$ for a reaction, it lets you calculate how the equilibrium constant will change with temperature. Conversely, if you can measure the equilibrium constant for a reaction at several temperatures, it lets you figure out $\Delta_r H^\circ$ *without* doing any calorimetry. Often this is easier than directly measuring the heat evolved from a reaction.

The Gibbs-Helmholtz equation There is a closely related equation, the Gibbs-Helmholtz equation, that gives the temperature dependence of G/T , or $\Delta G/T$:

$$\left(\frac{\partial G/T}{\partial T}\right)_P = \frac{-H}{RT^2}. \quad (7.87)$$

(You can put Δ s in front of both G and H there and get a result that is valid for changes such as chemical reactions at constant P and T .) The derivation of the Gibbs-Helmholtz equation is very similar to that of the van't Hoff equation. Your text will describe it.

7.8 Equilibrium in real gases and solutions

7.8.1 Definition of activity

For ideal gases we found that

$$\mu_i = \mu_i^\circ(T) + RT \ln \left(\frac{P_i}{P^\circ} \right) \quad (7.88)$$

and from that

$$\Delta G_T^\circ = \sum_i \nu_i \mu_i^\circ(T) = -RT \ln K_P^\circ \quad (7.89)$$

In dealing with reactions in condensed phases (especially solutions) and in real gases, it is useful to try to continue writing chemical potentials in that way. We define the (dimensionless) *activity* a_i of substance i such that

$$\mu_i = \mu_i^\circ(T) + RT \ln a_i, \quad (7.90)$$

where $\mu_i^\circ(T)$ is the chemical potential of substance i in some specified reference state (the “standard state”). The chemical potential of substance i itself, μ_i , does not depend on the choice of standard state; but since $\mu_i^\circ(T)$ clearly does, the activity a_i will as well.

With this definition of activity we find, by the same procedure as before, that there is an equilibrium constant with the form

$$K^\circ = \prod_i a_i^{\nu_i}. \quad (7.91)$$

This is now a general expression for an equilibrium constant, based on the general requirement for material equilibrium. The task of describing an equilibrium has now been converted to the task of finding appropriate values of the activities a for each system of interest.

Activities for ideal gases Simply by matching up Eq. (7.91) with our earlier expression for the ideal-gas equilibrium constant, you can see that for ideal gases, the activity of species i must be simply its partial pressure P_i divided by the standard state pressure P° . That is, the activity for an ideal gas is simply its partial pressure measured in units of the standard pressure.

7.8.2 Real gas activities: the fugacity

Eq. (7.90) applies to real gases as well as to solutions, but to preserve a concept of “effective pressure” in real gases, we define the *fugacity* f_i of a gas i such that

$$\mu_i = \mu_i^\circ(T) + RT \ln \left(\frac{f_i}{P^\circ} \right), \quad (7.92)$$

that is, $a_i = f_i/P^\circ$. The fugacity has units of pressure, and to make explicit the deviations from ideal gas behavior we write $f_i = \phi_i P_i$ where P_i is the true partial pressure of gas i and ϕ_i is the fugacity coefficient. Fugacity coefficients approach 1 at low gas density, so that the equilibrium properties of real gases become those of ideal gases at low density. The “standard state” for real gases is therefore not a real state, but an imaginary state where the gases are at pressures of 1 bar but behaving ideally.

Fugacity coefficients for pure gases can be calculated from

$$\ln \phi(P) = \int_0^P \left(\frac{Z(P') - 1}{P'} \right) dP' \quad (7.93)$$

where Z is the compression factor of the gas, $Z = \frac{PV_m}{RT}$. For gas mixtures, a first approximation (called the “Lewis-Randall rule”) is to set the fugacity coefficients for all gases in the mixture to those of the pure gases. If the intermolecular interactions between the different gases are very different, though, that is not a good approximation. Methods for calculating fugacity coefficients for mixtures are given in Reid, Prausnitz, and Poling, *The Properties of Gases and Liquids*, 4th edition (McGraw-Hill, 1987).

With fugacity coefficients in hand, we have

$$K^\circ = \prod_i \left(\frac{f_i}{P^\circ} \right)^{\nu_i} = \prod_i \left(\frac{\phi_i P_i}{P^\circ} \right)^{\nu_i}, \quad (7.94)$$

which can be factored to give

$$\frac{K^\circ}{\prod_i (\phi_i)^{\nu_i}} = \prod_i \left(\frac{P_i}{P^\circ} \right)^{\nu_i}. \quad (7.95)$$

A sensible way to evaluate equilibrium pressures in reacting real gas mixtures is as follows. You calculate K° in the usual way from tabulated values of $\Delta_f G_T^\circ$, and work out initial estimates of the equilibrium pressures by assuming all the gases are ideal. With the approximate equilibrium pressures thus obtained, you find fugacity coefficients of the mixture components, then “correct” K° by dividing by the appropriate quotient of fugacity coefficients of the reacting gases. After that, the equilibrium pressures in the reacting mixture can be found again. A couple of iterations of this procedure is usually enough to converge it, since the gas behavior is not usually very far from ideal.

7.8.3 Ideal and ideally dilute solutions

To define useful standard states for solution equilibrium calculations, we need to construct a solution equivalent of the ideal gas law. In an ideal gas, there are no

intermolecular interactions. The intermolecular interactions in liquid solutions are so important that it would be foolish to ignore them. Instead, we imagine two kinds of solutions in which the intermolecular interactions are simplified:

1. In an *ideal solution*, the interactions between species A and B are the same as those between A and A and those between B and B.
2. In an *ideally dilute solution*, there are so few B (solute) molecules that only A–A and A–B interactions exist; no B–B interactions need be considered.

A mixture of two similar liquids often makes a nearly ideal solution; for example, benzene and toluene, acetone and methyl ethyl ketone, or ethanol and isopropanol. An ideally dilute solution, on the other hand, generally must be very dilute (more so for electrolyte solutes), but there is no requirement that solute and solvent be chemically similar. Glucose in water can be an ideally dilute solution at low concentration, but is not an ideal one under any circumstances.

Raoult's Law

I will follow the convention of denoting properties of pure substances with asterisks. The chemical potential of pure liquid A (at some specified T and P) is μ_A^* . At liquid-vapor equilibrium, that must be equal to the chemical potential of pure vapor A, so we have (treating vapor A as an ideal gas)

$$\mu_A^* = \mu_A^\ominus + RT \ln \left(\frac{P_A^*}{P^\ominus} \right) \quad (7.96)$$

where μ_A^\ominus is the chemical potential of vapor A at the standard pressure, and P_A^* is the vapor pressure of pure A.

Now if we have a solution, with some B mixed in with the A, the chemical potential of A in the liquid changes, and its vapor pressure also changes (since at equilibrium the chemical potentials of A in the two phases must be the same.) We write

$$\mu_A = \mu_A^\ominus + RT \ln \left(\frac{P_A}{P^\ominus} \right) \quad (7.97)$$

Eliminating μ_A^\ominus between those two equations gives

$$\mu_A = \mu_A^* + RT \ln \left(\frac{P_A}{P_A^*} \right) \quad (7.98)$$

Now if you make a mixture of benzene and toluene, and measure the vapor pressure above the liquid, you do not get a value that is the sum of the vapor

pressures of the two pure substances. You would not expect to, since that would mean that if you put a very tiny amount of toluene into a benzene sample its vapor pressure would nearly double! Instead, you would expect that the vapor pressure above a nearly-pure benzene sample would be nearly that of benzene, and the vapor pressure above a nearly-pure toluene sample would be nearly that of toluene. In fact that is the case, and *Raoult's Law* is the statement that for ideal solutions, the vapor pressure above a mixed solution will vary linearly with the composition of the solution. More specifically,

$$P_A = x_A P_A^*, \quad (7.99)$$

where x_A is the mole fraction of A in the solution. Even for solutions that are not ideal, this expression gives a limiting behavior for the majority component as the solution becomes very dilute. That is, adding a small amount of solute to any solvent will change the vapor pressure of the solvent according to Eq. (7.99).

Substituting Eq. (7.99) into Eq. (7.98) gives

$$\mu_A = \mu_A^* + RT \ln x_A. \quad (7.100)$$

We will use this equation shortly to define activity coefficients for nonideal solutions.

Henry's Law

Raoult's Law gives the vapor pressure behavior for the solvent (the majority component) in the limit of high dilutions for real solutions. There is a corresponding limiting law for the solute (the minority component): the vapor pressure of the solute above the solution is still proportional to the mole fraction of solute, but the proportionality constant is not simply the vapor pressure of the pure solute. Instead, we write

$$P_B = x_B K_B, \quad (7.101)$$

where K_B is called the "Henry's Law constant" for the solute. The Henry's Law constant has units of pressure (it is sometimes defined in terms of the molality instead of the mole fraction, in which case it has units of bar mol kg^{-1}). It depends on the solvent and on the temperature, but only very weakly on pressure.

Henry's Law plays an important role in environmental chemistry, since it determines the partitioning of surface water contaminants between aqueous and gas phases. Henry's Law constants for many substances in water, and for fewer substances in other solvents, are available in tables; the NIST WebBook has Henry's Law constants in water for many compounds.

Figure 7.2 shows how Raoult's and Henry's Laws apply to a real solution in several cases. Raoult's Law works for the majority component and Henry's Law for the minority component at either extreme of solution composition, while neither works particularly well in between.

Figure 7.2: Vapor pressure behavior of real solutions. From Lewis and Randall, *Thermodynamics*, 2nd edition; original data from J. von Zawidzki, *Z. Phys. Chem* **35**, 129 (1900).

7.8.4 Activity conventions for solvents and solutes

Solvent activities

Eq. (7.98) was

$$\mu_A = \mu_A^* + RT \ln \left(\frac{P_A}{P_A^*} \right)$$

If the solution is ideal, then Raoult's Law holds, $P_A = x_A P_A^*$, and we have

$$\mu_A = \mu_A^* + RT \ln x_A. \quad (7.102)$$

But even if the solution is not ideal, we can write instead

$$\mu_A = \mu_A^* + RT \ln a_A, \quad (7.103)$$

with

$$a_A = \frac{P_A}{P_A^*}, \quad (7.104)$$

and everything still works. Now you can see that the activity a_A is a sort of "effective mole fraction"; if the solution is ideal, it is exactly the mole fraction, but if it is not, the activity is different from the mole fraction but can still be determined by measuring the partial pressure of A above the solution. To emphasize the limiting mole-fraction behavior, we can write

$$a_A = \gamma_A x_A, \quad (7.105)$$

where γ_A is an activity coefficient.

Example In an acetone-chloroform solution with the liquid mole fraction of acetone was 0.2003, the mole fraction of acetone in the vapor was 0.1434 and the total vapor pressure above the solution was 262 torr. At the same temperature, the vapor pressure of pure acetone is 344.5 torr. Let us evaluate the activity coefficient of acetone in the solution.

Leaving out subscripts, we have $a = P/P^*$, and $a = \gamma x$. The partial vapor pressure P of acetone is the total vapor pressure times the mole fraction of acetone in the vapor. Combining all those gives

$$\gamma = \frac{x_{\text{vapor}} P_{\text{tot}}}{x_{\text{liquid}} P^*} \quad (7.106)$$

$$= \frac{(0.1434)(262)}{(0.2003)(344.5)} \quad (7.107)$$

$$= 0.544 \quad (7.108)$$

The activity coefficient is less than one; the acetone is less likely to leave the solution and appear in the vapor than it would be in pure acetone. The attractive interactions between acetone and chloroform produce “negative deviations” from Raoult’s Law.

Activities calculated in the way I just showed are called Raoult’s Law activities, or “solvent activities”. Solvents are always treated this way, and in mixtures of liquids with relatively large mole fractions of both components this treatment might be used for both. This mole-fraction convention is always used for pure materials as well; this is the reason that in ordinary equilibrium constant expressions, we can leave out terms for the solvent or for any pure materials (like the solid at the bottom of a saturated solution in a solubility equilibrium problem).

In this convention, all the components of the solution are treated on an equal footing. Usually, though, there is a clear “solvent” and one or more “solutes” with much lower mole fractions. Next let us examine the usual convention for that case.

Solute activities

The difficulty with the Raoult’s Law convention for activities when solutes are considered is that the activity coefficients approach 1 as the mole fraction approaches 1, and that is very far from typical conditions for solutes. Were we to use that convention for solutes, we would be dealing with activity coefficients far from 1 most of the time, which would be painful. Instead, we model our activity coefficients on the ideally-dilute solution, which shows Henry’s Law behavior, and write

$$a_B = \frac{P_B}{K_B} \quad (7.109)$$

Note that we use the Henry’s Law constant this time, in place of the vapor pressure of the pure liquid. Once again we determine activity coefficients with vapor pressure measurements. The vapor pressure behavior of a solute obeys Henry’s Law in the limit of small mole fraction, so activity coefficients in this convention will approach 1 as the solute become more dilute. This definition for the activity is called (big surprise) the Henry’s Law convention.

7.8.5 Molality scale activities

In fact, in tables of thermodynamic functions, solution activities are usually given in terms of the molality (moles solute/kg solvent) scale rather than the mole fraction scale. This change makes a difference in the absolute values of the tabulated numbers but does not change the value of any ΔG or ΔH that you would calculate. We write

$$\mu_B = \mu_B^\circ + RT \ln \frac{b}{b^\circ}, \quad (7.110)$$

where b indicates the molality of the solution, b° is the “standard molality” (one mol/kg), and μ_B° is the chemical potential of B in the “molality-scale standard state”, which is a hypothetical state in which the concentration of B is 1 molal but it behaves as though it was at very high dilution.

7.8.6 Molar concentration scale activities

Similarly, some thermodynamic tables define their functions in terms of the molar concentration of a solute instead of the molality or mole fraction. In those, the standard state is a (hypothetical) state in which the solute is at a concentration of 1M but is behaving as though the solution was ideally dilute.

At high dilution, all three conventions for solute activities give the same numerical values for activity coefficients. As the concentration increases, the different definitions for activity coefficients diverge. You just have to look carefully to see which standard state your thermodynamic table uses! Then any equilibrium constant you calculate from the $\Delta_r G^\circ$ will be defined in terms of activities based on that scale.

7.8.7 Practical activity calculations

How do you actually use all this information about activities? We saw that in the real-gas case there was an equation that would give us the fugacities directly for real gases, and in some gas mixtures that’s good enough for practical work.

For binary solutions where both components are present in substantial quantity, we saw earlier how to calculate activity coefficients based on vapor pressure data.

When one component is definitely the minor one (the “solute”), if that component is volatile it’s still possible to get activities from vapor pressure measurements, from Eq. (7.109).

If, as is often the case, a nonelectrolyte solvent does not have enough vapor pressure to be measured, you can get its activity coefficients by measuring the vapor pressure of the *solvent* as a function of solute concentration, and using

the Gibbs-Duhem equation (E&R §9.5. The application to nonvolatile solutes is not described there, but is described in Levine, *Physical Chemistry* 6th edition, §10.4.).

For electrolytes, there is a relatively simple and successful formula (the Debye-Hückel limiting law; equation 10.32 in E&R) that can let you estimate activity coefficients for solvated ions directly at very low concentrations. For higher concentrations there are some empirical fitting laws, and tabulated data are extensive. Activity coefficients for electrolytes are often far from 1 even at relatively modest concentrations, and it's more important to include them for ionic reactions than for other solution reactions.

In each case, the practical application is similar to that I described in the real-gas case: you calculate an equilibrium constant from your thermodynamic data, you estimate final concentrations/molalities/ mole fractions assuming all the activity coefficients are 1, you then estimate (by the methods described above) a set of activity coefficients and “adjust” the equilibrium constant to account for them, then calculate a new set of final concentrations and go around until you converge.

7.8.8 Fractional distillation

Let's look at the distillation process for an ideal liquid-liquid solution. I want to introduce a “temperature-composition phase diagram” to help describe the qualitative behavior.

Consider an ideal binary solution at fixed total pressure; use the example of 1-propanol and 2-propanol. One component has a lower boiling point than the other. If the temperature of the mixture is lower than the lower boiling point, the system will be all liquid. If the temperature is higher than the higher boiling point, the system will be all vapor. At temperatures between those two, both liquid and vapor can exist.

Figure 7.3 shows the temperature-composition phase diagram. The region below the lower curve (the “boiling point curve”) is the all-liquid region. In between the two curves we can have both liquid and vapor. A horizontal (fixed- T) line connecting points on the lower and upper curves is called a *tie line*. The intersection of the tie line with the two curves gives the compositions of the liquid and vapor phases in equilibrium at that T .

It is important to realize that the x -axis on this diagram is the *total* or *bulk* or *average* mole fraction of the whole system, liquid and vapor together. This is different from the mole fraction x -axis we used in the discussion of Raoult's Law, which was the mole fraction in the liquid. In the region where the system is all liquid, of course the average mole fraction is that of the liquid; in regions where

the system is all vapor, the average mole fraction is that in the vapor. In regions where both liquid and vapor are present, the average mole fraction of the system will not equal either the liquid or vapor mole fractions.

Figure 7.3: Temperature-composition phase diagram for an ideal binary solution.

E&R section 9.3 shows you how to calculate the two curves point-by-point. The general formulas, derived easily from Raoult's Law, are

$$x_B^l = \frac{P_{\text{tot}} - P_A^*(T)}{P_B^*(T) - P_A^*(T)} \quad (7.111)$$

$$x_B^v = \frac{P_B^*(T)}{P_{\text{tot}}} \frac{P_{\text{tot}} - P_A^*(T)}{P_B^*(T) - P_A^*(T)} \quad (7.112)$$

Think about what happens when you distill a solution starting with the composition at point *A* in the diagram (about one-fourth mole fraction *B*). We heat the solution until we reach the boiling point of the mixture at point *A*. Then the liquid starts to boil. The vapor that first comes off has the composition at the other end of the tie line that begins at *A*, that is, it has the composition at point *B*,

which looks to be between two-thirds and three-quarters B. If we then condense some of that vapor, we get a solution at point *C*. Now if we boil that stuff and take off the first vapor that appears, we get the composition at point *D*, and so on.

If your two components have very similar boiling points, the two-phase region in the diagram will be very narrow, and it will take many successive evaporations and condensations to get to nearly pure B. On the other hand, if the two boiling points are very different, it may take only one or two stages to do the job. In that case, a rotovap or a simple Vigreux column may suffice.

Chapter 8

Statistical mechanics

Statistical mechanics, the last major field of physical chemistry, is the one that connects the molecular properties of the quantum world with the thermodynamic properties of the macroscopic world. Its task is to permit the calculation of macroscopic properties (pressure, equilibrium constants, boiling points, and so on) from the properties of the molecules themselves. It began with Maxwell and Boltzmann and the kinetic theory of gases, and took great strides with the work of Gibbs and Einstein. There is a large and busy research community now applying it to liquid and solid systems and especially to biological problems.

Statistical mechanics has two principal postulates:

1. We can calculate the time-averaged value of any macroscopic property of a single system by instead imagining very many similar systems (“similar” meaning with a sufficient set of macroscopic properties defined: for example, volume, temperature, and composition), and averaging over that collection of imagined systems. Such an average is called an average over the *ensemble*.
2. For a macroscopic system of specified volume, temperature, and composition, all quantum states of equal energy have equal probability of occurring.

With those two postulates you can get remarkably far. The quantity of central importance in statistical mechanics is the *partition function*:

$$Q = \sum_j e^{-E_j/k_B T}, \quad (8.1)$$

where the sum is over all quantum states (not energy levels; each state of a degenerate group is treated separately) of the macroscopic system, and E_j is the total energy of each state.

If the partition function is known (a nearly impossible condition in the general case), then all the thermodynamic properties of the system are calculable. For example:

$$U = k_B T^2 \left(\frac{\partial(\ln Q)}{\partial T} \right)_{V, N_i} \quad (8.2)$$

$$S = k_B T \left(\frac{\partial(\ln Q)}{\partial T} \right)_{V, N_i} + k_B \ln Q \quad (8.3)$$

$$A = -k_B T \ln Q \quad (8.4)$$

The actual calculation of partition functions for macroscopic systems of interacting particles (for example, liquids) is very difficult, because the number of possible quantum states of a system of many molecules is enormous. Practical calculations require approximations. Some very clever approaches are known, but let's move to noninteracting systems (ideal gases!) where concrete results are easier to come by.

8.1 Molecular partition functions

If we have a collection of identical, noninteracting molecules, then the overall partition function becomes

$$Q = \frac{q^N}{N!}, \quad (8.5)$$

where N is the number of molecules and q is the *molecular partition function*:

$$q = \sum_r e^{-\frac{\epsilon_r}{k_B T}}, \quad (8.6)$$

where r labels the individual quantum states of a single molecule, and ϵ_r is the energy of each level. The molecular partition function can be rewritten in terms of energy *levels*, as opposed to individual quantum states, giving

$$q = \sum_j g_j e^{-\frac{\epsilon_j}{k_B T}}, \quad (8.7)$$

where g_j is the degeneracy of level j with energy ϵ_j .

8.2 The Boltzmann distribution

One of the most fundamental results of molecular statistical mechanics is the Boltzmann distribution law. The probability of finding a molecule in energy level

i is given by

$$P_i = \frac{g_i e^{-\frac{\epsilon_i}{k_B T}}}{q} \quad (8.8)$$

For example, the fraction of molecules in a sample of CO at 300 K in the rotational level J is

$$P_J = \frac{(2J+1)e^{-\frac{BJ(J+1)}{k_B T}}}{\sum_{J=0}^{\infty} (2J+1)e^{-\frac{BJ(J+1)}{k_B T}}} \quad (8.9)$$

With $B = 1.9225 \text{ cm}^{-1}$, at 300 K we get $q = 106.9$ and $P(10) = 0.067$. To evaluate the partition function I carried out the sum up to $J = 50$, which is plenty high to converge the sum to three decimal places.

8.3 Equilibrium constants for gas reactions

The Boltzmann distribution extends in an interesting way even to chemical reactions. You can think of a reacting system as distributing its molecules among different states that actually have different chemical compositions. For example, in a sample of bromine gas at 500 K, some of the bromine molecules will be dissociated. The dissociated molecule has a higher energy (because energy had to be put in to break the bond) but also a higher degeneracy (because there are many more ways to have two atoms moving inside a container than to have a single molecule moving around; with the molecule, many possible motions that have the atoms far apart or moving in wildly different directions are impossible). Extension of the idea of the Boltzmann distribution to reacting ideal gases gives us a formula for the equilibrium constant of the reaction $aA + bB \rightleftharpoons cC + dD$ in terms of the molecular partition functions:

$$K_c(T) = \frac{(q_C/V)^c (q_D/V)^d}{(q_A/V)^a (q_B/V)^b} \quad (8.10)$$

To use this expression you must include all the relevant degrees of freedom (translational, rotational, vibrational, and electronic) in your molecular partition functions. Atoms in their ground states have only translational energies, though they usually have electronic degeneracies (2 for doublet states, 3 for triplet states, and so on.) Molecules, on the other hand, have all these sorts of energies, and it is also necessary to include the bond energies in the partition function. Over the next few days we will see how to compute the different factors in the molecular partition function for diatomic molecules, drawing on our earlier study of molecular quantum mechanics.

8.3.1 Rotational partition function for a heteronuclear diatomic

In the rigid rotor approximation, the energy levels of a rotor are given by $E_J = BJ(J+1)$, where B is the rotational constant (traditionally specified in cm^{-1}) and J is the rotational quantum number. The rotational level with quantum number J represents $2J+1$ degenerate states corresponding to different values of m_J . It is straightforward to insert that formula into the general expression for the partition function, giving

$$q_R = \sum_{J=0}^{\infty} (2J+1) \exp \frac{-BJ(J+1)}{k_B T}. \quad (8.11)$$

For most molecules at ordinary temperatures, that sum can be carried out directly (with a computer); by the time J reaches 100 or so, the terms become very small so the sum can be truncated without substantial loss of accuracy.

For most diatomics not including H atoms, a shortcut is available. The sum cannot be evaluated analytically. But, if the spacing between energy levels is small compared to $k_B T$, it is a good approximation to replace the sum by an integral, treating J as a continuous variable:

$$\sum_{J=0}^{\infty} (2J+1) \exp \frac{-BJ(J+1)}{k_B T} \approx \int_0^{\infty} (2J+1) \exp \frac{-BJ(J+1)}{k_B T} dJ. \quad (8.12)$$

It may seem surprising that turning a sum into an integral makes a problem easier, but in this case it does: the derivative of $J(J+1)$ is $(2J+1)dJ$, so that integral can be done analytically. The result is

$$q_R \approx \frac{k_B T}{B}. \quad (8.13)$$

Note that $k_B T$ and B must have the same units; if you have the usual B expressed in cm^{-1} , then the “Boltzmann constant in wavenumbers” $k_B/hc = 0.695 \text{ cm}^{-1}/\text{K}$ can be used directly.

This “high temperature” approximation is good for non-hydride diatomics at room temperature and above. You test it for CO in your homework. For hydrides, and especially for H_2 (with $B = 60 \text{ cm}^{-1}$), it’s not very good.

Homonuclear diatomics When a molecule contains two identical atoms, the partition function becomes a little more complicated. Because two orientations of the molecule look the same, the simple formula for the partition function produces a “double counting” of states, and it is necessary to divide q_R by a “symmetry number” σ . $\sigma = 2$ for homonuclear diatomics, and can have higher values for polyatomics.

8.3.2 Vibrational partition function for diatomics

If we treat the stretching of a diatomic molecule with the harmonic oscillator approximation, we have the simple formula $E_v = (v + 1/2)\hbar\omega$ for the energy levels. The energy levels are nondegenerate. The vibrational partition function is therefore

$$q_V = \sum_{v=0}^{\infty} \exp \left[\frac{-(v + 1/2)\hbar\omega}{k_B T} \right]. \quad (8.14)$$

That sum *can* be done analytically. We factor out the $1/2$ piece and rewrite the remainder as a geometric series:

$$q_V = \exp \left[\frac{-(1/2)\hbar\omega}{k_B T} \right] \sum_{v=0}^{\infty} \left(\exp \left[\frac{-\hbar\omega}{k_B T} \right] \right)^v \quad (8.15)$$

The exponential inside the sum is always < 1 , so the sum converges and can be evaluated with the geometric series formula $\sum_{i=0}^{\infty} r^i = \frac{1}{1-r}$, yielding

$$q_V = \frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}} \quad (8.16)$$

For diatomic molecules, you usually have information about the energy levels through the quantity $\hbar\omega/hc$, called either $\tilde{\nu}_0$ or ω_e depending on the source. It has units of cm^{-1} , so you need k_B in cm^{-1} as well.

For diatomics with light atoms and stiff bonds (HCl, N_2 , etc) $\hbar\omega/hc$ is on the order of $1500\text{--}3000 \text{ cm}^{-1}$, while $k_B T$ at room temperature is about 200 cm^{-1} . The excited vibrational levels will have almost no thermal population and q_V will be very close to 1. At elevated temperature or for heavier diatomics with weaker bonds (I_2 , several vibrational levels may be populated and the vibrational partition function may become larger. It also can be quite a bit larger than 1 for polyatomic molecules with many vibrational degrees of freedom.

8.3.3 Translational partition function

How are we to perform a sum over levels for translational motion, since those are not quantized for a free particle? And why would it matter?

It matters because in chemical reactions the total number of particles may change, and there are a *lot* more ways to arrange two particles moving in a container than only one. So the number of particles has an important effect on the overall probability of a state. To evaluate the translational partition function, we do something simple. We say the particle is contained in some sort of container (a flask or a room) and use the ordinary particle-in-a-box energy levels. Because

the box is large, the energy levels will be very close together and we expect that many of them will be populated.

For motion in just one dimension, if we assume a box length L , we have

$$E_n = \frac{n^2 h^2}{8mL^2}, \quad (8.17)$$

where n is the PIB quantum number (starting at 1) and m is the particle mass. The partition function is then

$$q_{T,1d} = \sum_{n=1}^{\infty} \exp \left[\frac{-n^2 h^2}{8mL^2 k_B T} \right]. \quad (8.18)$$

There's no hope of evaluating this sum directly: it has too many nonnegligible terms, because L is so large and h is so small. For example, if we assume an H atom in a 1-m box, the billionth term ($n = 10^9$) has the value $\exp(-3.3 \times 10^{-23}) \sim 1$; that is, the sum is nowhere near converging. We therefore must look for some better way.

In this case, the same trick used for the high-temperature approximation to the rotational partition function works. We can turn the sum into an integral, and the approximation is excellent because the energy levels are very closely spaced compared to $k_B T$. Collecting the constants into $\alpha = \frac{h^2}{8mL^2}$, we obtain

$$q_{T,1d} \approx \int_{n=0}^{\infty} \exp \left[\frac{-\alpha n^2}{k_B T} \right] dn. \quad (8.19)$$

That's an ordinary Gaussian integral. You knew how to do it six months ago. You might have forgotten: $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$. So we get

$$q_{T,1d} = \frac{1}{2} \sqrt{\frac{\pi k_B T}{\alpha}} \quad (8.20)$$

Substituting back in for α we find

$$q_{T,1d} = (2\pi m k_B T)^{1/2} L / h. \quad (8.21)$$

Sometimes that result is written in terms of the *thermal de Broglie wavelength* $\Lambda = h / \sqrt{2\pi m k_B T}$. The 1D translational partition function is then just $q_{T,1d} = L / \Lambda$.

Handling three dimensions is trivial; motions in the three directions are independent so the 3D partition function is just the cube of the 1D. Therefore (noticing $L^3 = V$, the volume)

$$q_T = \frac{L^3}{\Lambda^3} = (2\pi m k_B T)^{3/2} \frac{V}{h^3}. \quad (8.22)$$

8.3.4 Equilibrium constant for diatomic dissociation

Eq. (8.10) gave the “concentration-scale equilibrium constant” K_c . We convert that to the ordinary K_P with the usual ideal gas law expression $K_P = (k_B T)^{\Delta n_g} K_c$ where Δn_g is the change in the number of moles of gas in the reaction. The equilibrium constant for the reaction $X_2 \rightleftharpoons 2X$ then becomes

$$K_P = k_B T \frac{(q_{\text{Na}}/V)^2}{q_{\text{Na}_2}/V} \quad (8.23)$$

We now have all the pieces assembled for computation of the equilibrium constant for a gas-phase reaction among diatomics. There is one last problem: we need to measure the energies in our formulas for reactants and products from the same origin. In the case of a diatomic dissociating to two atoms, that’s fairly easy to handle: the difference between the “zero point” for the diatomic and the zero point for the atoms is just the dissociation energy ϵ_D of the diatomic. We should just add that amount of energy to all the atomic (product) energies. A constant added to all the energies factors out of the partition-function sum to give a term like $e^{-\epsilon_D/k_B T}$. So we end up with

$$K_P = k_B T \frac{(q_{\text{Na}}/V)^2}{q_{\text{Na}_2}/V} e^{-\epsilon_D/k_B T} \quad (8.24)$$

That equation can be used directly. For q_{Na} you need only translational and electronic molecular partition functions. For q_{Na_2} you need all four: q_T , q_R , q_V , and q_{el} .

There remains one more annoying detail. Values for ϵ_D come in two flavors: D_0 , the energy difference between $\nu = 0$ of the diatomic and the separate atoms, and D_e , the difference between the bottom of the diatomic potential well and the separated atoms. They are different by $\frac{1}{2}\hbar\omega$, the zero point energy of the diatomic. If you have D_e , then you use Eq. (8.16) for q_V . If you have D_0 , which leaves out the zero-point energy, then you also need a q_V that leaves out the zero-point energy. That energy is what produces the $e^{-\hbar\omega/2k_B T}$ numerator in Eq. (8.16), so the modified q_V is

$$q'_V = \frac{1}{1 - e^{-\hbar\omega/k_B T}} \quad (8.25)$$

And that’s it!

[two fists raised in triumph]