1 Fundamentals of Chemical Kinetics

1.1 Concentrations

Chemical kinetics is the quantitative study of chemical systems that are changing with time. (Thermodynamics, another of the major branches of physical chemistry, applies to systems at equilibrium—those that do not change with time.)

In this course, we will restrict our attention to systems that are homogeneous and well mixed (a major restriction), and that are at constant volume (a minor restriction that simplifies the notation, but can be easily lifted.) With these two restrictions it is useful to describe the chemical system in terms of *concentrations* of the species present:

$$[\mathrm{A}] = \frac{n_{\mathrm{A}}}{V} \tag{1}$$

where [A] indicates the concentration of species A, V is the volume, and n_{A} indicates the amount of A present in that volume. In discussions of reactions in solution, the usual units for [A] are mol dm^{-3} or mol/L, called molar and written M. (The name "molar" and the symbol M are now regarded as obsolete by NIST and by IUPAC, and the explicit notations mol dm^{-3} or mol/L are preferred; however, most chemists appear to be ignoring their lead.)

For gas phase reactions, the customary units are molecules cm^{-3}, often written simply cm^{-3}.

The chemical state of a homogeneous system can be described by specifying the concentrations of all the species present and the pressure and temperature.

1.2 Reaction rates

For a general chemical reaction

$$\mathrm{aA} + \mathrm{bB} + \ldots \longrightarrow \mathrm{yY} + \mathrm{zZ} + \ldots, \tag{2}$$

we define *specific reaction rates* with respect to each reactant or product:

$$r_\Gamma = \pm 1 \frac{1}{\gamma} \frac{d\Gamma}{dt}, \tag{3}$$

where γ is the stochiometric coefficient for species Γ in the balanced equation. The $+$ sign is used if Γ is a product, the $-$ sign if it is a reactant. Thus

$$r_{\mathrm{A}} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt}. \tag{4}$$

The rate always has units of concentration/time. For solution reactions the usual units are $\mathrm{M\,s^{-1}}$, while for gas phase reactions the most common unit is $\mathrm{cm^{-3}\,s^{-1}}$.

These specific rates are not necessarily the same for different species. *If* there are no reaction intermediates of significant concentrations, then

$$r_{\mathrm{A}} = r_{\mathrm{B}} = r_{\mathrm{Y}} = r_{\mathrm{Z}} = v, \tag{5}$$

the rate of the reaction. For very many systems, intermediates are important, all the specific rates are different, and it is then necessary to specify which specific rate is being discussed.

1.3 Rate laws

For most reactions, the rate(s) depend on the concentrations of one or more reactants or products. Then we write

$$r_{\Gamma} = f([\mathrm{A}], [\mathrm{B}], [\mathrm{Y}], [\mathrm{I}], [\mathrm{C}], T, p, \ldots) \tag{6}$$

where the list shows explicitly that r might depend on the concentrations of species other than those in the balanced equation, as well as on temperature, pressure, and so on. Often the dependence on variables other than concentrations is suppressed (a set of conditions is implied or specified), so that we write

$$r_{\Gamma} = f([\mathrm{A}], [\mathrm{B}], [\mathrm{Y}], [\mathrm{I}], [\mathrm{C}], \ldots). \tag{7}$$

This kind of expression, giving the rate of the reaction as a function of the concentrations of various chemical species, is called a *rate law.* Notice that the rate law is a differential equation: it gives the derivative (with respect to time) of one of the concentrations in terms of all the concentrations. The solution to such a differential equation is a function that gives the concentration of species Γ as a function of time.

1.3.1 Examples

The gas phase reaction that is the foundation of the very powerful infrared HBr laser is

$$\mathrm{H_2} + \mathrm{Br_2} \longrightarrow 2\mathrm{HBr}. \tag{8}$$

It has the rate law

$$\frac{1}{2}\frac{d[\mathrm{HBr}]}{dt} = \frac{k_1[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}}{1+\frac{[\mathrm{HBr}]}{k_2[\mathrm{Br_2}]}}, \tag{9}$$

where k_1 and k_2 are numbers (called *rate coefficients*, or sometimes *rate constants*) that are independent of the species concentrations but do depend on T.

The solution phase two-electron transfer reaction

$$2\mathrm{Fe}^{2+} + \mathrm{Tl}^{3+} \longrightarrow 2\mathrm{Fe}^{2+} + \mathrm{Tl}^{+} \tag{10}$$

has the rate law

$$\frac{1}{2}\frac{d[\mathrm{Fe}^{2+}]}{dt} = k[\mathrm{Fe}^{2+}][\mathrm{Tl}^{3+}]. \tag{11}$$

The gas phase reaction between hydrogen and chlorine,

$$\mathrm{H_2} + \mathrm{Cl_2} \longrightarrow 2\mathrm{HCl}, \tag{12}$$

is the basis of a popular demonstration (the "HCl cannon"). In the presence of oxygen it has the rate law

$$\frac{1}{2}\frac{d[\mathrm{HCl}]}{dt} = \frac{k_1[\mathrm{H_2}][\mathrm{Cl_2}]^2}{k_2[\mathrm{Cl_2}] + [\mathrm{O_2}]([\mathrm{H_2}] + k_3[\mathrm{Cl_2}])} \tag{13}$$

1.4 Simple rate laws and reaction order

In some cases, the rate law takes on the simple form

$$r_\Gamma = k[\mathrm{A}]^m[\mathrm{B}]^n[\mathrm{C}]^o\cdots, \tag{14}$$

proportional to powers of reactant concentrations. Then the sum of the powers is called the reaction order (or overall order), and the individual powers are called the orders with respect to the particular reactants. The orders m, n, o, etc., must be determined experimentally; neither the form of the rate law nor the orders (should they be defined at all) can be predicted from the balanced equation.

In the second example above, the overall reaction is second order: first order with respect to each of Fe^{2+} and Tl^{3+}.

The other two example reactions do not have rate laws of this simple form. Note, however, that they can appear to have simple forms under some circumstances. In the first example, if there is very little HBr present so that $k_2[\mathrm{Br_2}] \gg [\mathrm{HBr}]$, the second term in the denominator of the rate law will be negligible compared to 1 and the reaction will appear to have overall order 3/2 (first order with respect to hydrogen and one-half order with respect to bromine). In the third example, if there is no oxygen present, the second term in the denominator disappears and the reaction appears overall second order (first order with respect to both hydrogen and chlorine.)

2 Integration of simple rate laws

Generally the rate law for a reaction is determined by measurements of the concentrations of one or more species as a function of time. I will approach the problem backwards, first showing what concentration-vs-time behavior might be expected for several simple rate laws, then talking about how to design experiments to measure rates and how to extract rate laws from kinetic data.

2.1 First order reactions

While true first order reactions 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.

If the general reaction

$$\mathrm{aA} + \mathrm{bB} + \ldots \longrightarrow \mathrm{yY} + \mathrm{zZ} + \ldots \tag{15}$$

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 the rate law is

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]. \tag{16}$$

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.

2.1.1 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:

$$\frac{1}{a}\frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k\,dt \tag{17}$$

$$\frac{1}{a}\int\frac{1}{[\mathrm{A}]}\,d[\mathrm{A}] = -k\int dt \tag{18}$$

$$\frac{1}{a}\ln[\mathrm{A}] = -kt + C \tag{19}$$

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

$$[\mathrm{A}](t) = e^{aC}e^{-akt} = C'e^{-k't}. \tag{20}$$

Most authors absorb the constant a into the first order rate coefficient k in order to avoid writing k'. It is important to pay attention to exactly what differential equation is being solved; sometimes those missing constants cause errors when people aren't careful.

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

$$[\mathrm{A}](t) = A_0e^{-k't} \tag{21}$$

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

Since a is known (it's part of the chemical equation), the rate coefficient can be determined by measuring [A] as a function of time.Figure 1 shows two common plots used to demonstrate or analyze this behavior.

2.1.2 Half life and time constant

The *half-life* for a reaction is time 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, they're the same.) For a first-order reaction we can find the half-life $t_{1/2}$ by substituting into Eq. (20):

$$[\mathrm{A}](t_{1/2}) = \frac{A_0}{2} = A_0e^{-k't_{1/2}} \tag{22}$$

$$\ln\frac{1}{2} = -k't_{1/2} \tag{23}$$

$$t_{1/2} = \frac{\ln 2}{k'} \tag{24}$$

Figure 1: Two plots showing the concentration-vs-time behavior for a simple first order reaction.

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 $1/e(\approx 0.37)$ of its initial concentration. We can find it by a similar calculation:

$$[\mathrm{A}](\tau) = \frac{A_0}{e} = A_0 e^{-k'\tau} \tag{25}$$

$$\ln\frac{1}{e} = -k'\tau \tag{26}$$

$$\tau = \frac{1}{k'} \tag{27}$$

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.

2.1.3 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: $Q = \alpha[\mathrm{A}] + \beta$), 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

$$Q = Ce^{-kt} + D, \tag{28}$$

and if A is a product you fit to

$$Q = C(1 - e^{-kt}) + D, \tag{29}$$

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

Many textbooks will suggest that you use the equation

$$-\ln\left(\frac{Q - Q_\infty}{Q_0 - Q_\infty}\right) = kt \tag{30}$$

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. In the homework solution set for this week I demonstrate both kinds of fits for one problem.

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 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

$$2\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \tag{31}$$

with the rate law

$$-\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}]. \tag{32}$$

This rate law is second order overall, and its rate coefficient k has units M^{-1} 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

$$-\frac{1}{2}\frac{d[\mathrm{A}]}{dt} \approx k'[\mathrm{A}], \tag{33}$$

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 much 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).

2.3 Reactions second order in a single reactant

Here we have

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]^2 \tag{34}$$

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -k\,dt \tag{35}$$

$$\int \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -k\int dt \tag{36}$$

$$-\frac{1}{[\mathrm{A}]} = -kt + C \tag{37}$$

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

$$\frac{1}{[\mathrm{A}]} - \frac{1}{A_0} = kt \tag{38}$$

The textbook analysis is to plot $1/[\mathrm{A}]$ 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

$$t_{1/2} = \frac{1}{kA_0} \tag{39}$$

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 (I show a couple of examples in the homework.)

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 simple reaction

$$a\mathrm{A} + b\mathrm{B} \longrightarrow \text{products}, \tag{40}$$

if A and B are consumed simultaneously we have

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = k[\mathrm{A}][\mathrm{B}]. \tag{41}$$

If A and B start with stoichiometric concentrations, $aA_0 = bB_0$, then this looks just like the previous case, since $a[\mathrm{A}] = b[\mathrm{B}]$ at all times.

Otherwise, we have two differential equations: one each in [A] and [B]. Since A and B are consumed simultaneously we can say

$$[\mathrm{B}] = B_0 - \frac{b}{a}\left(A_0 - [\mathrm{A}]\right), \tag{42}$$

so that

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]\left(B_0 - \frac{b}{a}\left(A_0 - [\mathrm{A}]\right)\right) \tag{43}$$

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]\left(aB_0 - bA_0 + b[\mathrm{A}]\right) \tag{44}$$

$$= k[\mathrm{A}]\left(\Delta_0 + b[\mathrm{A}]\right) \tag{45}$$

This equation is separable; solving it, applying the initial condition, and substituting back in for [B] gives

$$\ln\left(\frac{[\mathrm{B}]}{[\mathrm{A}]}\right) = \ln\left(\frac{B_0}{A_0}\right) + k\Delta_0 t. \tag{46}$$

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

The closer A_0 and B_0 are to stoichiometric concentrations, the more poorly Δ_0 is known; 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.

3 Determination of rate laws

I will first discuss two popular methods that assume a rate law of the simple form

$$\text{rate} = k[A]^m[B]^n[C]^o \cdots \tag{47}$$

Both usually require that a single reactant be *isolated*; that is, its concentration must be the only one in the rate law that is changing during the reaction. Usually reactants are isolated by flooding the system with the other reactants.

3.1 Method of half-lives

We have already seen a few examples of this technique. If you compare the first half-life for a reaction with the second half-life, the ratio gives you the order according to Table 1. (I derived this table with a method exactly like the one required for Problem 25.21 in Atkins.)

Table 1 Ratios of second to first half-lives for reactions of various orders. The first half-life is the time require for the limiting reactant to reach half its initial concentration; the second half-life if the time required for it to go from half its initial concentration to one-fourth of its initial concentration.

Order	0	1/2	1	3/2	2	3
$t_{1/2}(2)/t_{1/2}(1)$	1/2	$1/\sqrt{2}$	1	$\sqrt{2}$	2	4

3.2 Method of Guess-and-Try

Here you do what you have been doing in the homework: take a guess at the reaction order (perhaps with the half-life method as a guide), and then make some sort of plot that should be a straight line if your guess was right. We have already worked out what plots you would make for three common rate laws, and several more are given in the table from Laidler's book on the next page.

There are a couple of problems with this method:

1. The rate law might not have a simple form at all.
2. You might get tired before guessing the right form, and decide that one of the ones you have already done seems to fit the data "okay", not realizing that another rate law (that you didn't try) fits much better.

If you use this method on a reaction you are studying, it is a good idea to check the result with one of the more detailed methods I describe in the next section. Also, it is very important to collect your data for long enough. Following the reaction out through at least two half-lives is necessary. It is very hard to distinguish an order 3/2 reaction from a first or second order one by looking at a plot that only takes the reaction halfway to completion.

3.3 Differential methods

The term "differential method" indicates that a derivative (a reaction rate) is being measured directly. To measure a rate, you measure concentrations at several times whose separation is small compared to the reaction half-life, then evaluate the derivative (the slope) $d[\mathrm{A}]/dt$ over that small region. If you make this measurement right at the beginning of the reaction, when the concentrations are the ones you put in the beaker, you are using the *initial rates* method; if you make rate measurements at several times while the reaction is going on, you are using the *single-run differential* method (these are Laidler's names.) The best kind of kinetic study uses these methods together.

3.3.1 Initial rates

To do an initial rates study you start the reaction several times with different starting concentrations. The concentrations are chosen so that several (at least two, but preferably three or more) runs are available in which the concentration of one reactant varies while the others stay the same. If you have n reactants and you want to use m concentrations for each then you will have to start the reaction $n(m-1)+1$ times.

Then, for each set of data that has one reactant changing and the others constant, you make a plot of the log of the initial rate (on the y axis) against the log of the initial concentration (on the x axis). The slope of this line gives you the order of the reaction with respect to that reactant. If the plot is not linear, then the reaction has no order with respect to that reactant (the rate law is not the simple product-of-powers form). This case is quite difficult to discover with other methods.

Note that in initial rates studies it is not necessary to flood the system with the other reactants; you do the measurements before any of the concentrations have changed anyway. Figure 2 (taken from Laidler) shows how the data look for a typical initial rate study on the order with respect to one reactant.

Figure 2: Figure from Laidler, *Chemical Kinetics* 3rd edition, showing treatment of initial rate data.

The initial rates method is the best general method for the determination of reaction orders. Its disadvantages are that (1) it can be time-consuming and expensive, since a rather large amount of data must be collected, and (2) it requires that the mixing and analytical methods be fast on the timescale of the reaction.

3.3.2 The single-run differential method

In this method, rates are taken from a single plot of concentration vs. time, where other concentrations than the one being studied are held constant (typically by flooding). At each of several times during the reaction, you measure the slope of the concentration-versus-time curve, and then make a plot of log of rate against log of concentration to obtain the order. The next page shows such an analysis on a reaction that turned out to be second order.

3.3.3 Combined differential methods

It is sometimes (when the rate law involves only one reactant, or when you can flood the others) possible to combine data from the initial rates and single run methods onto a single plot. If you are doing an initial rates study, you have to start the reaction a bunch of times anyway, and if it doesn't take too long you might as well follow the concentrations for a while. Then you can make a plot of $\ln v$ vs. $\ln c$ that includes all the data.

If the single-run data lie along the line given by the initial rates, then the rate law is simple. If the single-run slopes are larger than the initial rate slope (as in the example plot below), then the reaction is slowing down more than expected as it progresses; it is *product inhibited.* If the single-run slopes are smaller than the initial rate slope, the reaction is not slowing down as much as expected; products are speeding it up somehow, and we say that it is *autocatalytic.*

4 Elementary Reactions and Mechanisms

If a chemical equation describes an *individual molecular event*, as for instance

$$O + CH_4 \longrightarrow OH + CH_3, \tag{48}$$

then we can write down the rate law from the stoichiometry:

$$-\frac{d[O]}{dt} = -\frac{d[CH_4]}{dt} = \frac{d[OH]}{dt} = \frac{d[CH_3]}{dt} = k[O][CH_4], \tag{49}$$

where k is an elementary rate constant. This example is a *bimolecular* reaction; the other possibilities are unimolecular and termolecular, both of which are rarer. Most chemical reactions are not elementary as written. One of the main goals of most kinetic studies is to determine the sequence of elementary reactions, or *mechanism*, which makes up an overall reaction.

The "laboratory" reaction

$$2ICl + H_2 \longrightarrow I_2 + 2HCl \tag{50}$$

might have the observed rate law

$$\frac{1}{2}\frac{d[HCl]}{dt} = k[ICl][H_2]. \tag{51}$$

This rate law *suggests* that the kinetics are dominated by a bimolecular reaction between ICl and H_2. One possibility for the mechanism is

$$ICl + H_2 \xrightarrow{k_1} HI + HCl \qquad \text{(slow)} \tag{52}$$

$$HI + ICl \xrightarrow{k_2} HCl + I_2 \qquad \text{(fast)} \tag{53}$$

We will shortly see how to analyze the behavior of this mechanism quantitatively. Note that adding together Eq. (52) and Eq. (53) gives the overall reaction.

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 mechanism (proposed) cannot be proven correct, though it can be proven wrong by disagreement with observed behavior.

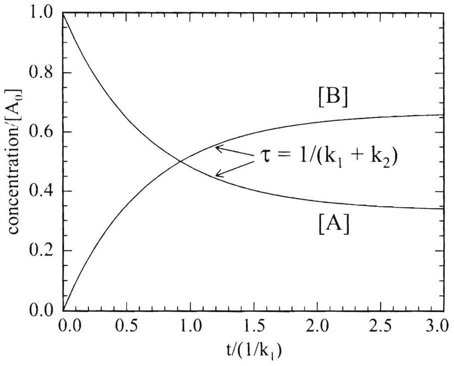

Figure 3: Behavior of a reversible first order reaction for the case $B_0 = 0$ and $k_1 = 2k_2$.

4.1 Simple example: reversible unimolecular transformation

The mechanism

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{54}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{A}, \tag{55}$$

which can also be written

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}, \tag{56}$$

gives the set of "elementary rate laws"

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_2[\mathrm{B}] \tag{57}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{58}$$

This is a system of two coupled ODEs. Once the initial conditions are specified, its solution describes the complete time dependence. Figure 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: $[\mathrm{B}] = B_0 + (A_0 - [\mathrm{A}])$ from stoichiometry, so that

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_2(B_0 + A_0 - [\mathrm{A}]). \tag{59}$$

Eq. (59) is now a separable differential equation in [A] only. Its solution, with $[\mathrm{A}](t=0) = A_0$, is

$$[\mathrm{A}](t) = \frac{1}{k_1 + k_2}\left\{(k_1A_0 - k_2B_0)e^{-(k_1+k_2)t} + k_2(A_0 + B_0)\right\} \tag{60}$$

The rate law in this case looks like

$$\begin{aligned} -\frac{d[\mathrm{A}]}{dt} &= (k_1 + k_2)[\mathrm{A}] - k_2(\mathrm{B}_0 + \mathrm{A}_0) && (61)\\ &= k'[\mathrm{A}] + C, && (62) \end{aligned}$$

and the reaction order is not defined.

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

$$\begin{aligned} k_1[\mathrm{A}]_{\mathrm{eq}} &= k_2[\mathrm{B}]_{\mathrm{eq}} && (63)\\ \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} &= \frac{k_1}{k_2} && (64)\\ &= K_{\mathrm{eq}} && (65) \end{aligned}$$

Many exact solutions of this type are given by G. Szabo, in *Comprehensive Chemical Kinetics*, ed. by Bamford and Tipper. (v.2?)

5 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.

5.1 Consecutive first-order reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{66}$$

An example of this sort of system is the electronic quenching of excited bromine atoms by CO_2,

$$\begin{aligned} \mathrm{Br}^*_{\frac{1}{2}} + \mathrm{CO}_2 &\longrightarrow \mathrm{CO}_2^*(001) + \mathrm{Br}_{\frac{3}{2}} && (67) \\ \mathrm{CO}_2^* + \mathrm{CO}_2 &\longrightarrow 2\mathrm{CO}_2, && (68) \end{aligned}$$

under conditions of excess CO_2 so that it is pseudo first order. One way to monitor the reaction progress is to measure IR luminescence of Br^* or CO_2^*.

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 $d[\mathrm{B}]/dt$, you get a "first order linear" (not separable) differential equation. It can be solved by standard techniques. [B] grows, then decays:

$$[\mathrm{B}] = \frac{k_1 \mathrm{A}_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{69}$$

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 4.

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

In this case, then at short times ($t \gtrsim 0$), the second exponential term in Eq. (69) is near 1, the equation looks like $\mathrm{B} \approx A_0(1 - e^{-k_1 t})$, and B grows in with time constant $1/k_1$ as though no conversion to C was occuring. At

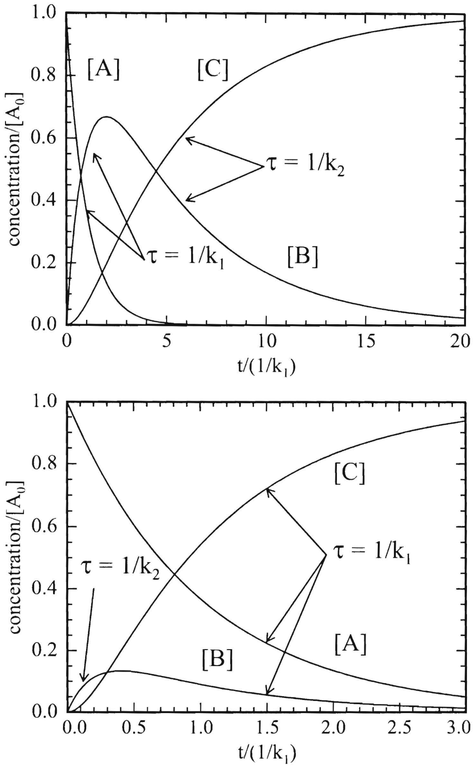

Figure 4: Temporal behavior of consecutive, irreversible first-order reactions. The upper panel shows the case $k_1 = 5k_2$; the lower panel shows the case $k_2 = 5k_1$.

long times, the first of the two exponential terms goes toward zero, and we have $[\mathrm{B}] \simeq A_0 e^{-k_2 t}$, 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: $[\mathrm{C}] = A_0 - [\mathrm{A}] - [\mathrm{B}]$.

5.1.2 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"

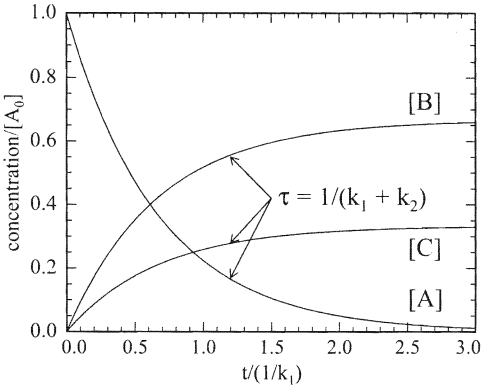

Figure 5: Temporal behavior of competing, irreversible first-order reactions. In this figure $k_1 = 2k_2$.

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.

5.2 Competitive (parallel) first order reactions

In this case, the mechanism is

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{70}$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{C} \tag{71}$$

The rate equations are

$$\frac{d[\mathrm{A}]}{dt} = -(k_1 + k_2)[\mathrm{A}] \tag{72}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] \tag{73}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{A}] \tag{74}$$

The first of the three is an ordinary first-order decay, giving $[\mathrm{A}] = A_0 e^{-(k_1+k_2)t}$. Substituting that result into the second and third equations gives separable equations for both B and C, which have nearly the same solutions:

$$[\mathrm{B}] = \frac{k_1 A_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t}) \tag{75}$$

$$[\mathrm{C}] = \frac{k_2 A_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t}) \tag{76}$$

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

5.2.1 Kinetic vs. thermodynamic control

If the reactions are reversible,

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{77}$$

$$\mathrm{A} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}, \tag{78}$$

then the issue of thermodynamic or kinetic control of products appears. Assuming no direct interconversion of B and C,

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{C}]_{\mathrm{eq}}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \cdot \frac{[\mathrm{A}]_{\mathrm{eq}}}{[\mathrm{C}]_{\mathrm{eq}}} = \frac{k_1}{k_{-1}} \frac{k_{-2}}{k_2} = K_{\mathrm{BC}}. \tag{79}$$

If $k_1 k_{-2} \ll k_{-1} k_2$ so that $K_{\mathrm{BC}} \ll 1$, 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 $[\mathrm{B}]/[\mathrm{C}] \approx k_1/k_2$. 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

$$\begin{array}{ll} k_1 = 10^0\,\mathrm{s}^{-1} & k_{-1} = 10^{-7} \\ k_2 = 10^{-2} & k_{-2} = 10^{-12} \end{array}$$

then Table 2 shows the resulting concentrations. This is a not-too-extreme case of kinetic control.

Table 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

5.2.2 Relative Rate Experiments

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

$$\mathrm{A_1 + B} \xrightarrow{k_1} \mathrm{P_1} \tag{80}$$

$$\mathrm{A_2 + B} \xrightarrow{k_2} \mathrm{P_2} \tag{81}$$

If B is added to a *mixture* of A_1 and A_2, whose concentrations are $\gg [\mathrm{B}]_0$, then

$$\frac{d[\mathrm{P_1}]}{dt} = k_1[\mathrm{A_1}]_0[\mathrm{B}] \tag{82}$$

$$\frac{d[\mathrm{P_2}]}{dt} = k_2[\mathrm{A_2}]_0[\mathrm{B}] \tag{83}$$

$$\frac{d[\mathrm{P_1}]}{d[\mathrm{P_2}]} = \frac{k_1[\mathrm{A_1}]_0}{k_2[\mathrm{A_2}]_0} \tag{84}$$

So, after a long time

$$\frac{[\mathrm{P_1}]_\infty}{[\mathrm{P_2}]_\infty} = \frac{k_1[\mathrm{A_1}]_0}{k_2[\mathrm{A_2}]_0} \tag{85}$$

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 A_1 and A_2, 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 ($C_6H_5\cdot$) by pyrolysis of a precursor, in the presence of both a hydrocarbon RH and CCl_4. After the reaction, measure the ratio $[C_6H_5Cl]/[C_6H_6]$. That ratio times $\frac{[\mathrm{RH}]_0}{[\mathrm{CCl_4}]_0}$ gives the ratio of rate constants $k_{\mathrm{CCl_4}}/k_{\mathrm{RH}}$. Careful work requires several starting ratios; then from Eq. (85) plotting the final product ratio vs. the initial reactant ratio yields k_1/k_2 as the slope, and a zero intercept.

Equivalently, the loss rates for A_1 and A_2 can be observed, if one is confident that no other processes remove them from the system. Then

$$\frac{d[\mathrm{A_1}]}{dt} = k_1[\mathrm{A_1}][\mathrm{B}] \tag{86}$$

$$\frac{d[\mathrm{A_2}]}{dt} = k_2[\mathrm{A_2}][\mathrm{B}]. \tag{87}$$

so

$$\frac{d[\mathrm{A}_1]}{d[\mathrm{A}_2]} = \frac{k_1}{k_2}\frac{[\mathrm{A}_1]}{[\mathrm{A}_2]} \tag{88}$$

$$k_2\frac{d[\mathrm{A}_1]}{[\mathrm{A}_1]} = k_1\frac{d[\mathrm{A}_2]}{[\mathrm{A}_2]} \tag{89}$$

$$k_2 \ln[\mathrm{A}_1] = k_1 \ln[\mathrm{A}_2] + \mathrm{C} \tag{90}$$

When $[\mathrm{A}_1] = [\mathrm{A}_1]_0$, $[\mathrm{A}_2] = [\mathrm{A}_2]_0$, so $\mathrm{C} = k_2 \ln[\mathrm{A}_1]_0 - \mathrm{k}_1 \ln[\mathrm{A}_2]_0$

$$k_2 \ln\left(\frac{[\mathrm{A}_1]}{[\mathrm{A}_1]_0}\right) = k_1 \ln\left(\frac{[\mathrm{A}_2]}{[\mathrm{A}_2]_0}\right) \tag{91}$$

$$\frac{k_1}{k_2} = \frac{\ln\left(\frac{[\mathrm{A}_1]}{[\mathrm{A}_1]_0}\right)}{\ln\left(\frac{[\mathrm{A}_2]}{[\mathrm{A}_2]_0}\right)} \tag{92}$$

so measurement of $[\mathrm{A}_1]$ and $[\mathrm{A}_2]$ at any time will give k_1/k_2.

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.

6 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 are only interested in reactants or products or both. So we seek a method to eliminate the concentrations of intermediates in our rate expressions.

Example:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{93}$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{\mathrm{k}_2} \mathrm{D} \tag{94}$$

Net reaction A + C → D.

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}] \tag{95}$$
$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - (k_{-1} + k_2[\mathrm{C}])[B] \tag{96}$$
$$\frac{d[\mathrm{C}]}{dt} = -k_2[\mathrm{B}][\mathrm{C}] \tag{97}$$
$$\frac{d[\mathrm{D}]}{dt} = k_2[\mathrm{B}][\mathrm{C}] \tag{98}$$

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

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{dt}} \approx 0. \tag{99}$$

This is called the steady-state or Bodenstein approximation.

We then use that assumption to eliminate [B] from the rate expressions for the product D.

$$\frac{d[\mathrm{B}]}{dt} \overset{\mathrm{SSA}}{\approx} 0 = k_1[\mathrm{A}] - (k_{-1} + k_2[\mathrm{C}])[\mathrm{B}] \tag{100}$$
$$[\mathrm{B}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{A}]}{k_{-1} + k_2[\mathrm{C}]} \tag{101}$$
$$\frac{d[\mathrm{D}]}{dt} \overset{\mathrm{SSA}}{\approx} \frac{k_1 k_2[\mathrm{A}][\mathrm{C}]}{k_{-1} + k_2[\mathrm{C}]} \tag{102}$$

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

$$\frac{d[\mathrm{D}]}{dt} \overset{\mathrm{SSA}}{\approx} \frac{k_1 k_2}{k_{-1}}[\mathrm{A}][\mathrm{C}] \qquad \text{apparent 2nd order} \tag{103}$$

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

$$\frac{d[\mathrm{D}]}{dt} \overset{\mathrm{SSA}}{\approx} k_1[\mathrm{A}] \qquad \text{apparent 1st order} \tag{104}$$

6.1 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

$$(k_{-1} + k_2[\mathrm{C}]) \gg k_1. \tag{105}$$

(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 $\frac{d[\mathrm{B}]}{dt} \approx 0$ must be incorrect. This period is over when

$$(k_{-1} + k_2[\mathrm{C}])t \gtrsim 5. \tag{106}$$

6.2 Other Simplifying Approximations

Once again, consider the mechanism

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{107}$$

$$B \xrightarrow{k_2} C \tag{108}$$

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

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] \tag{109}$$

$$\frac{d[B]}{dt} = k_1[A] - (k_{-1} + k_2)[B] \tag{110}$$

$$\frac{d[C]}{dt} = k_2[B] \tag{111}$$

I want to consider two main cases, illustrated in Figure 6 and summarized in Table 3.

Table 3 Relations among simplifying approximations.

Case	Requirements	Long-time rate coefficient
SSA	$(k_{-1} + k_2) \gg k_1$	$k_1k_2/(k_{-1} + k_2)$
REA	$(k_1 + k_{-1}) \gg k_2$	$k_1k_2/(k_1 + k_{-1})$
SS-EQ	$k_{-1} \gg k_1$ and $k_{-1} \gg k_2$	k_1k_2/k_{-1}

6.2.1 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 4.1. 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

$$\frac{d[C]}{dt} \overset{\text{REA}}{\approx} \frac{k_1k_2}{k_{-1}}[A] \tag{112}$$

This is the "rapid equilibrium approximation."

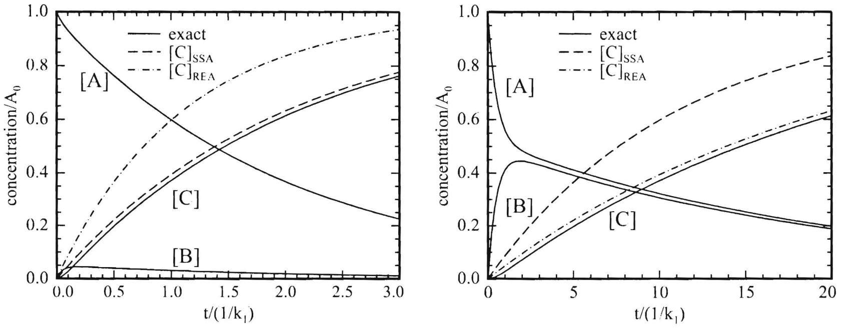

Figure 6: The steady-state and equilibrium approximations for the $A \rightleftharpoons B \longrightarrow C$ mechanism, for two different sets of rate coefficients. In the left panel $k_{-1} = k_2 = 10k_1$; in the right panel $k_1 = k_{-1} = 10k_2$.

6.2.2 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

$$\frac{d[\mathrm{B}]}{dt} = -k_1[\mathrm{A}] - (k_{-1} + k_2)[\mathrm{B}] \overset{\mathrm{SSA}}{\approx} 0 \tag{113}$$

so

$$[\mathrm{B}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{A}]}{(k_{-1} + k_2)} \tag{114}$$

$$\frac{d[\mathrm{C}]}{dt} \overset{\mathrm{SSA}}{\approx} \left(\frac{k_1 k_2}{k_{-1} + k_2}\right)[\mathrm{A}] \tag{115}$$

6.2.3 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 3.

6.3 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 $A \longrightarrow C$ 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 ports of a mechanism which 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.

6.4 Examples

6.4.1 Ligand substitution

The nucleophilic substitution reaction

$$\mathrm{Ni(CO)_4 + PPh_3 \longrightarrow Ni(CO)_3PPh_3 + CO} \tag{116}$$

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

$$\mathrm{Ni(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(CO)_3 + CO} \tag{117}$$

$$\mathrm{Ni(CO)_3 + PPh_3 \xrightarrow{k_2} Ni(CO)_3PPh_3} \tag{118}$$

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

$$\frac{d}{dt}[\mathrm{Ni(CO)_3}] = k_1[\mathrm{Ni(CO)_4}] - (k_{-1}[\mathrm{CO}] + k_2[\mathrm{PPh_3}])[\mathrm{Ni(CO)_3}] \tag{119}$$

$$[\mathrm{Ni(CO)_3}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{Ni(CO)_4}]}{k_{-1}[\mathrm{CO}] + k_2[\mathrm{PPh_3}]} \tag{120}$$

$$\frac{d}{dt}[\mathrm{Ni(CO)_3PPh_3}] = k_2[\mathrm{Ni(CO)_3}][\mathrm{PPh_3}] \tag{121}$$

$$\overset{\mathrm{SSA}}{\approx} k_2[\mathrm{PPh_3}]\frac{k_1[\mathrm{Ni(CO)_4}]}{k_{-1}[\mathrm{CO}] + k_2[\mathrm{PPh_3}]} \tag{122}$$

Under conditions of high ligand ($\mathrm{PPH_3}$) concentration, the rate law will reduce to

$$\frac{d}{dt}[\mathrm{Ni(CO)_3PPh_3}] \approx k_1[\mathrm{Ni(CO)_4}], \tag{123}$$

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

6.4.2 Dinitrogen pentoxide decomposition

The reaction

$$\mathrm{2N_2O_5 \rightarrow 4NO_2 + O_2} \tag{124}$$

follows an observed first-order rate law. The reaction between $\mathrm{N_2O_5}$ and NO also looks first order but is much faster. $\mathrm{NO_3}$, a blue gas, also appears as

Figure 7: Data on dinitrogen pentoxide decomposition (from Johnston, *Gas Phase Reaction Rate Theory*).

an intermediate. A page from Johnston showing some data is reproduced in Figure 7.

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

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3 \tag{125}$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO + NO_2 + O_2 \tag{126}$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2 \tag{127}$$

We shall try to find an expression for $\frac{d[NO_2]}{dt}$.

$$\frac{d[NO_2]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] + 2k_3[NO][NO_3] \tag{128}$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - (k_{-1} + k_2)[NO_2][NO_3] - k_3[NO][NO_3] \tag{129}$$

Apply SSA to NO_3:

$$\frac{d[NO_3]}{dt} \overset{\text{SSA}}{\approx} 0 \tag{130}$$

$$[NO_3] \overset{\text{SSA}}{\approx} \frac{k_1[N_2O_5]}{(k_{-1} + k_2)[NO_2] + k_3[NO]} \tag{131}$$

Substitute into $\frac{d[NO_2]}{dt}$ expression:

$$\frac{d[NO_2]}{dt} \overset{\text{SSA}}{\approx} k_1[N_2O_5]\left\{1 - \frac{k_1[NO_2] + -2k_3[NO]}{(k_{-1} + k_2)[NO_2] + k_3[NO]}\right\} \tag{132}$$

$$\frac{d[NO_2]}{dt} \overset{\text{SSA}}{\approx} k_1[N_2O_5]\left\{\frac{k_2[NO_2] + 3k_3[NO]}{(k_{-1} + k_2)[NO_2] + k_3[NO]}\right\} \tag{133}$$

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

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] \overset{\text{SSA}}{\approx} 0 \tag{134}$$

$$[NO] \overset{\text{SSA}}{\approx} \frac{k_2}{k_3}[NO_2] \tag{135}$$

so

$$\frac{d[\mathrm{NO_2}]}{dt} \overset{\mathrm{SSA}}{\approx} k_1[\mathrm{N_2O_5}]\left\{\frac{k_2[\mathrm{NO_2}]+3k_2[\mathrm{NO_2}]}{(k_{-1}+2k_2)[\mathrm{NO_2}]}\right\} \tag{136}$$

$$\frac{d[\mathrm{NO_2}]}{dt} \overset{\mathrm{SSA}}{\approx} \frac{4k_1k_2}{k_{-1}+2k_2}[\mathrm{N_2O_5}] \tag{137}$$

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.

6.4.3 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

$$\mathrm{Br_2 + N_3^-} \xrightarrow{\text{fast}} \mathrm{BrN_3 + Br^-} \tag{138}$$

$$\mathrm{BrN_3 + Br^-} \xrightleftharpoons{\mathrm{K_1}} \mathrm{Br_2N_3^-} \tag{139}$$

$$\mathrm{BrN_3 + N_3^-} \xrightarrow{\mathrm{k_1}} \mathrm{Br^- + N_6} \tag{140}$$

$$\mathrm{N_6} \xrightarrow{\mathrm{k_3}} \mathrm{3N_2} \tag{141}$$

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 dependended linearly on $[N_3^-]$. The intermediate N_6 is an obvious candidate for the steady state approximation:

$$[\mathrm{N_6}] \overset{\mathrm{SSA}}{\approx} \frac{k_1}{k_3}[\mathrm{BrN_3}][\mathrm{N_3^-}] \tag{142}$$

$$\frac{d[\mathrm{N_2}]}{dt} = 3k_3[\mathrm{N_6}] \tag{143}$$

$$\overset{\mathrm{SSA}}{\approx} 3k_1[\mathrm{BrN_3}][\mathrm{N_3^-}] \tag{144}$$

The first reaction is "fast", so it is reasonable to regard the initially added bromine as converted completely to $\mathrm{BrN_3}$ immediately. The $\mathrm{BrN_3}$ can either be complexed by $\mathrm{Br^-}$ in step 139, or react to form product in step 140. The equilibrium gives us

$$[\mathrm{Br_2N_3^-}] \overset{\mathrm{REA}}{\approx} K_1[\mathrm{BrN_3}][\mathrm{Br^-}] \tag{145}$$

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.

$$\begin{aligned} M &= [\mathrm{BrN_3}] + [\mathrm{Br_2N_3^-}] && (146)\\ &\overset{\mathrm{REA}}{\approx} [\mathrm{BrN_3}] + K_1[\mathrm{BrN_3}][\mathrm{Br^-}] && (147)\\ &\overset{\mathrm{REA}}{\approx} [\mathrm{BrN_3}](1 + K_1[\mathrm{Br^-}]) && (148)\\ [\mathrm{BrN_3}] &\overset{\mathrm{REA}}{\approx} \frac{M}{1 + K_1[\mathrm{Br^-}]} && (149)\end{aligned}$$

Since M is only destroyed in step Eq. (140),

$$\begin{aligned} \frac{dM}{dt} &= -k_1[\mathrm{BrN_3}][\mathrm{N_3^-}] && (150)\\ &\overset{\mathrm{REA}}{\approx} -k_1[\mathrm{N_3^-}]\frac{M}{1 + K_1[\mathrm{Br^-}]} && (151)\end{aligned}$$

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 $[\mathrm{N_3^-}]$ and [Br]. The effective first-order rate coefficient is

$$k_{\mathrm{eff}} = [\mathrm{N_3^-}]\frac{k_1}{1 + K_1[\mathrm{Br^-}]}. \tag{152}$$

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 $\mathrm{Br_2N_3^-}$. The standard experimental analysis of this sort of competitive equilibrium is to measure k_{eff} at several values of $[\mathrm{Br^-}]$, and make a plot of $[\mathrm{N_3^-}]/k_{\mathrm{eff}}$ against $[\mathrm{Br^-}]$. 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 $Br_3N_3^{2-}$, 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.

7 Experimental Techniques

7.1 Elementary considerations

Several questions must be answered before an experimental approach can be selected.

- Over what time does the reaction occur?
- Are the reactants stable or unstable?
- What range of temperature is interesting?

All these questions are relevant to the choice of experimental technique independent of the particular detection method employed.

7.2 Stable reactants, slow to medium time scales

7.2.1 Batch mixing

This is kinetics on classical stir-in-a-pot reactions. It works for $\tau \gtrsim 10\,\mathrm{s}$. You can analyze the concentrations by removing samples at intervals and titrating, using GC, whatever. A method for stopping reaction in your sample (freezing, neutralization, etc) is handy. Or, you can monitor the reaction *in situ* - optical absorption, polarimetry, ion-selective electrodes, conductivity, etc. all work.

7.2.2 Flow Experiments

For faster reactions, say $\tau \gtrsim 0.1$ s, you can let the reactants come together continuously in some sort of mixing chamber, then allow them to react while flowing along a tube. At each point along the tube, the concentrations are steady, so signals can be averaged to get good signal to noise; experiments at different distances along the flow tube yield concentrations at different times since the reaction began. One disadvantage is that it usually requires lots of reactants.

Discharge flow experiments for gas phase reactions with unstable reactants use a steady electric discharge to produce one or both reactants before they enter the main reaction tube. This is a very popular method for studying reactions of radical and ionic species. Spectroscopic detection along the length of the tube, or mass spectrometry at the end of the flow tube, using a moveable injector to vary the flow distance, are the most popular detection

Figure 8: Simple flow apparatus.

techniques. Gas phase flow experiments can have time resolution down to ~ 0.1 ms, though at that speed they consume prodigous amounts of gases. Good references are C.J. Howard, J. Phys. Chem. **83**, 3 (1979), and F. Kaufman, J.Phys. Chem. **88**, 4909 (1984).

Oser et al, 24th Symp. (International) on Combustion, The Combustion Institute, 1992) studied $OH + CH_3$ reactions by generating OH and CH_3 in separate discharges:

$$\begin{aligned}
H_2 &\xrightarrow{\mu\text{wave}} 2H && \tag{153}\\
H + NO_2 &\longrightarrow OH + NO && \text{fast,} \tag{154}\\
F_2 &\xrightarrow{\mu\text{wave}} 2F && \tag{155}\\
F + CH_4 &\longrightarrow CH_3 + HF && \text{fast,} \tag{156}\\
OH + CH_3 &\longrightarrow H_2O + CH_2 && \text{(plus other channels)} \tag{157}
\end{aligned}$$

They measured the rate coefficient of the last reaction by detecting OH at different distances along the flow tube with fluorescence.

7.2.3 Stopped-flow technique

For faster reactions, 10^{-3} s or slower, the stopped-flow technique works for solution samples. In this method, solutions of reactants are mixed rapidly in a special chamber and flowed through a detection cell (optical detection is most popular). So long as the reactants are flowing steadily, no change in the composition of the mixture in the detection chamber appears. When the flow is stopped suddenly, the composition begins changing and this change is monitored in time. See Figure 9.

Stopped flow is popular among enzyme kineticists, especially for studying enzyme reactions in the initial stages before the steady state concentrations of enzyme-substrate complex have formed. The term for work during this buildup period in the enzyme community is "transient state kinetics", in contrast to "steady state kinetics" when the Michaelis-Menten analysis works.

Figure 9: Schematic of stopped-flow apparatus

The hydrodynamics of most solvents limits the stopped-flow technique to timescales of a millisecond or longer; faster reactions will already be partially underway by the time the mixing is complete, so it is hard to get meaningful data on well-mixed solutions. For faster reactions of stable species, it is necessary to produce one reactant *in situ*, or to use near-equilibrium techniques.

7.3 Near-equilibrium methods for fast reactions

Two kinds of near-equilibrium techniques are important: relaxation and nmr. Both are good on the microsecond to millisecond timescale.

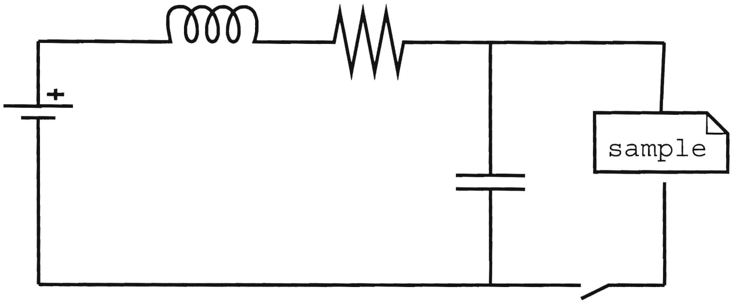

Figure 10: Schematic of T-jump apparatus

7.3.1 Relaxation (T-jump and p-jump, mostly)

Let reaction come to equilibrium, with concentrations A_e, B_e, Z_e for A + B $\rightleftharpoons$ Z. Then "disturb" the equilibrium by changing T, P, etc. suddenly so that the equilibrium concentrations should be different, and watch the relaxation to a new equilibrium value.

Relaxation example: A + B $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ Z

$$k_1 A_e B_e = k_{-1} Z_e \tag{158}$$

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}][\mathrm{B}] + k_{-1}[\mathrm{Z}] \tag{159}$$

Write

$$[\mathrm{A}] = A_e - \delta, [\mathrm{B}] = B_e - \delta, [\mathrm{Z}] = Z_e + \delta \tag{160}$$

$$\frac{d[\mathrm{A}]}{dt} = -\frac{d\delta}{dt} = -k_1(A_e - \delta)(B_e - \delta) + k_{-1}(Z_e + \delta) \tag{161}$$

$$-\frac{d\delta}{dt} = -k_1(A_eB_e - (A_e + B_e)\delta + \delta^2) + k_{-1}Z_e + k_{-1}\delta \tag{162}$$

$$-\frac{d\delta}{dt} = \delta(k_1(A_e + B_e) + k_{-1} - k_1\delta) \underbrace{-k_1 A_e B_e + k_{-1} Z_e}_{=0} \tag{163}$$

If $\delta \ll A_e + B_e$ (a "small" disturbance), then

$$\frac{d\delta}{dt} \approx -(k_1(A_e + B_e) + k_{-1})\delta, \tag{164}$$

and all components relax toward their equilibrium concentrations with first-order kinetics, $\tau = \frac{1}{k_1(A_e+B_e)+k_{-1}}$. Together with long-time measurements of the equilibrium concentrations, both k_1 and k_{-1} can be obtained.

The most common ways to disturb the equilibrium are to change T or P rapidly. To change T, the solution can be heated with an electric current. Figure 10 shows a basic circuit. The energy stored in a capacitor of capacitance C at voltage V is $\frac{1}{2}CV^2$. When the switch is closed, the energy stored on the capacitor heats the solution resistively, so $\Delta T = \frac{1}{2}C_V^{-1}CV^2$, where C_V is the heat capacity of the solution.

To change P for a pressure-jump experiment, the usual technique is to burst a diaphragm holding back a high-pressure gas. For slow reactions, concentration-jump also works: add an aliquot of product to shift equation back toward reactants, etc.

Manfred Eigen won the 1967 Nobel Prize in Chemistry for development of the relaxation method of studying fast reactions. (It was shared with the developers of the flash photolysis method to be described shortly.)

7.3.2 NMR Lineshape Analysis (Espenson sec. 11.5)

Chemical shifts in nmr spectra are determined by "chemical environments" of the nuclei at resonance. Consider $(CH_3)_2NCHO$. It has a hindered rotation about the C-N bond. If that rotation is "frozen", the two methyl groups are in different environments, and the spectrum (of either ^1H or ^{13}C) will show a pair of lines, one for each methyl group. However, if the rotation is very fast compared to the time over which the absorption experiments, each methyl group will see an "average" environment that is part -H and part -O, and so they will have exactly the same chemical shift and appear as a single nmr line. In between these two extremes, the lines show a continuous change of behavior. An analysis of the lineshape can therefore be used to determine the rate of exchange. Figure 11 shows a nice set of data recently obtained by Professors Matchett and Zhang.

The "experimental timescale" is given roughly by $1/\Delta\nu$, where $\Delta\nu$ is the difference in asborption frequencies in the absence of exchange. Typically the timescales range from 100 μs to 1 s.

Generally these experiments are done at varying temperatures, to change the rates. A rough guide is that the two lines will just become distinct at a temperature where $k \sim \frac{\pi}{\sqrt{2}}(\Delta\nu)$ (for $K_{\text{eq}} = 0.5$.) Most new nmr spectrometers contain canned software to do these lineshape analyses.

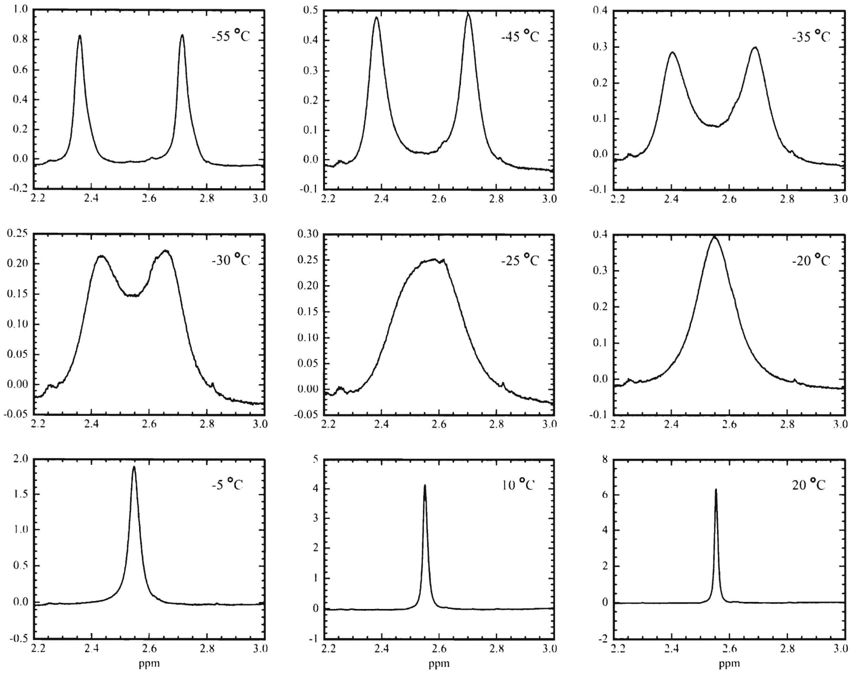

Figure 11: NMR lineshapes obtained by Profs. Matchett and Zhang. The two resonance lines correspond to two protons at the end of a substituted ethylene; they are mixed by rotation about the C-C double bond.

Several different kinds of reactions can be studied with nmr. They include solvent exchange, as in

$$\mathrm{CH_3CH_2OH^a + H_2^bO \rightleftharpoons CH_3CH_2OH^b + H^aOH^b} \tag{165}$$

Here the methyl and ethyl protons are slightly split by the hydroxyl proton, because the OH proton can have its moment aligned along or against the magnetic field. However, when an exchange reaction occurs, the new proton can go on in either direction. If many exchanges occur, the CH_3CH_2 protons see only an average OH-proton indirect coupling.

Electron transfer and metal-ligand equilibria can also be studied effectively this way.

In these experiments, as in the relaxation (T-jump, P-jump, etc.) methods for studying equilibrium rates, the "relaxation constant" $k' = k_1 + k_{-1}$

is measured. The individual rates can be obtained if the equilibrium constant k_1/k_{-1} is also known.

References on lineshape analysis include E.L. King, J. Chem. Ed. **56**, 580 (1979), and H. Günther, *NMR Spectroscopy - An Introduction*, Wiley, NY, 1972.

7.4 Flash Photolysis

Flash photolysis is the main technique for medium-to-fast reactions with unstable reactants, and is nearly the only technique used for the very fastest reactions. It uses photochemistry of a "precursor" P to produce reactant A:

$$\text{P} \xrightarrow{h\nu} \text{A (+ other stuff)} \tag{166}$$

$$\text{A} + \text{B} \longrightarrow \text{products} \tag{167}$$

The photolysis step needs to be fast compared to subsequent reaction steps. Flashlamps give light pulses lasting 1–20 μs; lasers can produce pulses of many lengths, but the most common ones nowadays range from 20 ns, adequate for bimolecular gas phase reactions at moderate pressure or bimolecular solution reactions (that do not have solvent as one reactant), down to about 50 fs, which is needed for the fastest unimolecular reactions in solution. The detection method also needs to be fast with respect to the overall kinetics; optical methods (transient absorption, laser-induced fluorescence, pulsed polarimetry) are the most popular approaches. In most experiments the flash and subsequent analysis are done repeatedly, either on the same sample if product buildup is not a problem, or on a series of fresh samples produced by a slow flow of reactants through the detection region.

Norrish and Porter shared the Nobel Prize in 1967 with Eigen, largely for their development of flash photolysis. The prize to Ahmed Zewail last year was for applications of flash photolysis at very short time scales.

A gas phase example is in Bersohn et al, J. Chem. Phys. **101**, 5818 (1994):

$$\text{SO}_2 \xrightarrow{\text{193nm, 10ns}} \text{SO} + \text{O}(^3P) \tag{168}$$

$$\text{O}(^3P) + \text{C}_2\text{H}_2 \longrightarrow \text{HCCHO}^* \tag{169}$$

$$\text{HCCHO}^* \longrightarrow \text{H} + \text{HCCO} \tag{170}$$

$$\text{HCCHO}^* \longrightarrow \text{CH}_2 + \text{CO} \tag{171}$$

Bersohn et al. monitored the H and CO products with laser induced fluorescence.

7.5 Shock Tube Experiments

In a shock tube experiment, a low-pressure gas of reactants is suddenly heated by the passage of a strong shock wave, produced by rupture of a diaphragm that was holding back a high pressure "driver" gas. The temperature can change by more than 1000 K in fractions of a millisecond, and optical techniques are used to follow the subsequent chemistry. This technique is good for gas phase reactions at high temperature (700-2500 K), and is nearly the only technique for gas phase reactions above $\approx$ 1400 K. Many of the rate coefficients needed in complicated models of hydrocarbon combustion have been measured this way.

Figure 12: Shock tube apparatus.

There are only about a dozen shock-tube laboratories in the world. The main disadvantages of the technique are

- The high-temperature chemistry is often very complicated, and it can be difficult to sort out different elementary reactions.
- It is hard to do repetitive signal averaging since each repetition of the experiment takes at least an hour or so. Experimenters are therefore limited to detecting species that are easy to see.

There was a good review of shock tube techniques and results by J.V. Michael, in the 1992 Ann. Rev. Phys. Chem.

8 Construction of candidate mechanisms from rate laws

8.1 Rate controlling steps in sequential mechanisms

The heuristic procedures I will describe below for constructing a mechanism from a carefully determined rate law depend on particular elementary steps being rate-controlling under some conditions. I therefore need to say a little more about how to think about rate controlling steps. *Intermediates* are stable chemical species at free energy minima; transition states are unstable and will immediately react without further perturbation.

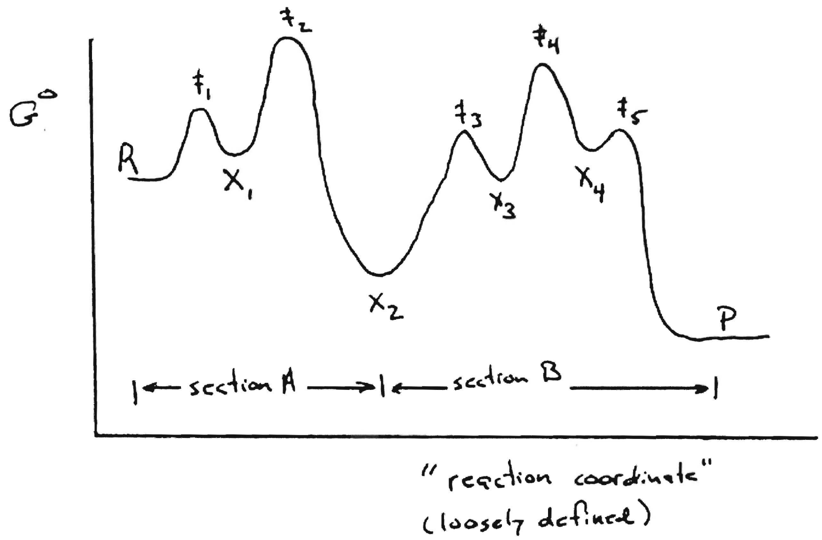

Figure 13: Schematic free energy diagram for sequential 1st-order system with 4 intermediates, A $\rightarrow X_1 \rightarrow X_2 \rightarrow X_3 \rightarrow X_4 \rightarrow$ P

In a sequential mechanism, to decide on an RCS you must divide the reaction path into sections separated by successively lower (more stable) intermediates. Condense the mechanism to include only those intermediates. Figure 13 shows the free-energy curve for a reaction that is a complicated sequence of first-order steps.

In Figure 13 we have

$$A \longrightarrow X_2 \longrightarrow P. \tag{172}$$

The other steps will be fast compared to those. Of the remaining steps, the one with the largest free energy barrier between the beginning and end of the *section* will be the RCS.

In Figure 13, the largest barrier is from X_2 to $\ddagger_4$, so the second step in the condensed scheme will be the RCS. Intermediate X_2 will build up; other intermediates will remain at low concentrations.

For bimolecular reactions, this simple scheme must be modified to include concentrations, producing "effective first-order" rate coefficients. See J.R. Murdoch, *J. Chem. Educ.* **58**, 32 (1981).

8.2 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 which 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. They are not foolproof but are sensible and useful.

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 6.4.2,

   $$2N_2O_5 \longrightarrow 4NO_2 + O_2, \tag{173}$$

   with rate law

   $$\frac{d[N_2O_5]}{dt} = k[N_2O_5], \tag{174}$$

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

   In the aqueous redox reaction

   $$Tl^{3+} + Hg_2^{2+} \longrightarrow Tl^{+} + 2Hg^{2+}, \tag{175}$$

$$\text{rate} = k\frac{[\text{Tl}^{3+}][\text{Hg}_2^{2+}]}{[\text{Hg}^{2+}]}. \tag{176}$$

We "subtract 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:

$$2(\text{Mn}^{\text{III}}\text{MG})^+ + \text{S}_2\text{O}_4^{2-} \longrightarrow 2(\text{Mn}^{\text{II}}\text{MG}) + 2\text{SO}_2, \tag{177}$$

where MG is the protein myoglobin, has the rate law

$$\text{rate} = k[(\text{Mn}^{\text{III}}\text{MG})^+][\text{S}_2\text{O}_4^{2-}]^{\frac{1}{2}}, \tag{178}$$

and the TS is thought to have the composition Mn MG SO_2 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.

$$3\text{I}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \longrightarrow \text{I}_3^- + 2\text{H}_2\text{O} \tag{179}$$

$$\frac{d[\text{I}_3^-]}{dt} = k_a[\text{I}^-][\text{H}_2\text{O}_2] + k_b[\text{I}^-][\text{H}_2\text{O}_2][\text{H}^+] \tag{180}$$

This acid-catalyzed reaction would be studied by monitoring the formation of I_3^- 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 $(H_2O_2I)^-$ and H_3O_2I.

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

$$\text{A} + \text{B} \underset{\text{k}_{-1}}{\overset{\text{k}_1}{\rightleftharpoons}} \text{C} \tag{181}$$

$$\text{C} + \text{A} \xrightarrow{\text{k}_2} \text{D} \tag{182}$$

$$\text{C} \xrightarrow{\text{k}_3} \text{D} \tag{183}$$

Applying SSA to C,

$$0 \overset{\text{SSA}}{\approx} \frac{d[\text{C}]}{dt} = k_1[\text{A}][\text{B}] - (k_{-1} + k_3 + k_2[\text{A}])[\text{C}] \tag{184}$$

so

$$[\mathrm{C}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{A}][\mathrm{B}]}{k_{-1} + k_3 + k_2[\mathrm{A}]} \tag{185}$$

Now

$$\frac{d[\mathrm{D}]}{dt} = k_2[\mathrm{A}][\mathrm{C}] + k_3[\mathrm{C}] \tag{186}$$

$$= \frac{k_1 k_2[\mathrm{A}]^2[\mathrm{B}]}{k_{-1} + k_3 + k_2[\mathrm{A}]} + \frac{k_1 k_3[\mathrm{A}][\mathrm{B}]}{k_{-1} + k_3 + k_2[\mathrm{A}]} \tag{187}$$

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

$$\mathrm{rate} = \left(\frac{\mathrm{k_1 k_2}}{\mathrm{k_{-1} + k_3}}\right)[\mathrm{A}]^2[\mathrm{B}] + \left(\frac{\mathrm{k_1 k_3}}{\mathrm{k_{-1} + k_3}}\right)[\mathrm{A}][\mathrm{B}] \tag{188}$$

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

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

$$\mathrm{rate} = k_1[\mathrm{A}][\mathrm{B}] + \frac{k_1 k_3}{k_2}[\mathrm{B}] \tag{189}$$

We can manipulate this expression to show that the first term dominates:

$$k_2 \cdot \mathrm{rate} = k_1 k_2[\mathrm{A}][\mathrm{B}] + k_1 k_3[\mathrm{B}] \tag{190}$$

$$= k_1[\mathrm{B}](k_2[\mathrm{A}] + k_3) \tag{191}$$

$$\approx k_1[\mathrm{B}]k_2[\mathrm{A}] \qquad \text{(from large [A] assumption)} \tag{192}$$

$$\mathrm{rate} = k_1[\mathrm{A}][\mathrm{B}] \tag{193}$$

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.

$$2\mathrm{Fe}^{2+} + \mathrm{Tl}^{3+} \rightarrow 2\mathrm{Fe}^{3+} + \mathrm{Tl}^{+} \tag{194}$$

$$-\frac{d[\mathrm{Tl}^{3+}]}{dt} = \frac{k[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{[\mathrm{Fe}^{2+}] + k'[\mathrm{Fe}^{3+}]} \tag{195}$$

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

$$\text{rate} = \frac{k}{k'} \frac{[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{[\mathrm{Fe}^{3+}]}. \tag{196}$$

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 $(\mathrm{FeTl})^{5+}$ and $(\mathrm{FeTl})^{4+}$.

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:

$$\mathrm{Fe}^{2+} + \mathrm{Tl}^{3+} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{Fe}^{3+} + \mathrm{Tl}^{2+} \tag{197}$$

$$\mathrm{Tl}^{2+} + \mathrm{Fe}^{2+} \xrightarrow{\mathrm{k}_2} \mathrm{Fe}^{3+} + \mathrm{Tl}^{+} \tag{198}$$

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

$$\frac{d[\mathrm{Tl}^{2+}]}{dt} = k_1[\mathrm{Fe}^{2+}][\mathrm{Tl}^{3+}] - [\mathrm{Tl}^{2+}](k_{-1}[\mathrm{Fe}^{3+}] + k_2[\mathrm{Fe}^{2+}]) \tag{199}$$

   so

$$[\mathrm{Tl}^{2+}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{Fe}^{2+}][\mathrm{Tl}^{3+}]}{k_{-1}[\mathrm{Fe}^{3+}] + k_2[\mathrm{Fe}^{3+}]} = \frac{k[\mathrm{Fe}^{2+}][\mathrm{Tl}^{3+}]}{[\mathrm{Fe}^{3+}] + k^1[\mathrm{Fe}^{2+}]} \tag{200}$$

$$\text{rate} = k_2[\mathrm{Tl}^{2+}][\mathrm{Fe}^{2+}] = \frac{k_1 k_2[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{k_{-1}[\mathrm{Fe}^{3+}] + k_2[\mathrm{Fe}^{2+}]} \tag{201}$$

$$\text{rate} = \frac{k[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{k'[\mathrm{Fe}^{3+}] + [\mathrm{Fe}^{2+}]} \tag{202}$$

   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.

8.3 Application of "mechanism rules" to a simple inorganic example

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

$$2V^{3+} + 2Hg^{2+} \longrightarrow 2V^{4+} + Hg_2^{2+} \tag{203}$$

The observed rate law is

$$-\frac{d[V^{3+}]}{dt} = \frac{k[V^{3+}]^2[Hg^{2+}]}{k'[V^{4+}] + [V^{3+}]}. \tag{204}$$

Rule 3 tells us to expect at least 2 steps. Rule 1 gives the composition of the two transition states as $(VHg)^{4+}$ and $(VHg)^{5+}$. 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 ($(VHg)^{5+}$), it's natural to bring them together as one step:

$$V^{3+} + Hg^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V^{4+} + Hg^{+} \tag{205}$$

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.

$$Hg^{+} + V^{3+} \xrightarrow{k_2} V^{4+} + Hg^{0} \tag{206}$$

$$Hg^{0} + Hg^{2+} \xrightarrow{k_3} Hg_2^{2+} \tag{207}$$

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

$$\frac{d[\mathrm{Hg}^+]}{dt} = k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}] - k_{-1}[\mathrm{V}^{4+}][\mathrm{Hg}^+] - k_2[\mathrm{V}^{3+}][\mathrm{Hg}^+] \tag{208}$$

$$[\mathrm{Hg}^+] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}]}{k_{-1}[\mathrm{V}^{4+}] + k_2[\mathrm{V}^{3+}]} \tag{209}$$

$$-\frac{d[\mathrm{V}^{3+}]}{dt} \overset{\mathrm{SSA}}{\approx} k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}] - k_{-1}[\mathrm{V}^{4+}][\mathrm{Hg}^+] + k_2[\mathrm{V}^{3+}][\mathrm{Hg}^+] \tag{210}$$

$$= k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}] + [\mathrm{Hg}^+](k_2[\mathrm{V}^{3+}] - k_{-1}[\mathrm{V}^{4+}]) \tag{211}$$

$$\begin{aligned} &= k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}] \\ &\quad + \left(\frac{k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}]}{k_{-1}[\mathrm{V}^{4+}] + k_2[\mathrm{V}^{3+}]}\right)(k_2[\mathrm{V}^{3+}] - k_{-1}[\mathrm{V}^{4+}]) \end{aligned} \tag{212}$$

$$= k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}]\left(1 + \frac{\left(k_2[\mathrm{V}^{3+}] - k_{-1}[\mathrm{V}^{4+}]\right)}{k_{-1}[\mathrm{V}^{4+}] + k_2[\mathrm{V}^{3+}]}\right) \tag{213}$$

$$= k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}]\left(\frac{2k_2[\mathrm{V}^{3+}]}{k_{-1}[\mathrm{V}^{4+}] + k_2[\mathrm{V}^{3+}]}\right) \tag{214}$$

$$= \frac{2k_1[\mathrm{V}^{3+}]^2[\mathrm{Hg}^{2+}]}{\frac{k_{-1}}{k_2}[\mathrm{V}^{4+}] + [\mathrm{V}^{3+}]} \tag{215}$$

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.

9 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 small compared to the distances between and the size of the container
3. The particles do not interact except that they have elastic (translational-energy-conserving) collisions with each other and the container walls
4. The particles move according to classical mechanics.

(Atkins, section 1.3, leaves out the last assumption.)

9.1 Pressure of an ideal gas

Consider a gas of N identical particles in a rectangular container. We want to calculate from kinetic theory the pressure the gas exerts on the walls.

Consider a single particle, particle i, with components of its velocity v_{xi}, v_{yi}, v_{zi}. Upon colliding elastically with a wall parallel to the yz plane, the x component of its velocity changes sign. The change in momentum of the particle is therefore $2mv_{xi}$, where m is the particle mass.

Now consider how many molecules will hit the wall in time Δt. All molecules within $v_x\Delta t$ of the wall, and that are moving toward the wall rather than away from it, will hit the wall in time Δt. Half the molecules are moving toward the wall, so the number that will hit the wall is $\frac{1}{2}NAv_x\Delta t/V$, where A is the area of the wall. The total momentum change at the wall is therefore

$\frac{1}{2}NAv_x\Delta t(2mv_x)/V = NAmv_x^2\Delta t/V$. Not all the molecules have the same x component of velocity, so I should use the average squared speed in that expression: $\Delta p = NAm\langle v_x^2\rangle\Delta t/V$. The force is the rate of change of momentum, $F = dp/dt$; the force on the wall is therefore the momentum change Δp divided by Δt, or $NAm\langle v_x^2\rangle/V$. The pressure is the force per unit area, so it is that force divided by the area of the wall: $P = Nm\langle v_x^2\rangle/V$.

There is nothing special about the x-direction; we should expect the average speeds of the molecules in all directions to be the same. If I call the average squared speed (in three dimensions) c^2, I have $c^2 = v_x^2 + v_y^2 + v_z^2$, and since all three directions are equivalent this reduces to $c^2 = 3v_x^2$ so we have

$$P = \frac{1}{3}\frac{Nmc^2}{V} \tag{216}$$

This gives the pressure of the gas in terms of microscopic properties of the molecules (their masses and average squared speed).

9.2 Average speed, translational energy, and temperature

I have used c^2 as the average of the square of the speed for the gas molecules. Then the average translational energy must be $\langle \varepsilon_{\text{tr}} \rangle = \frac{1}{2}mc^2$. For the whole sample of N particles we therefore have $E_{\text{tr}} = \frac{1}{2}Nmc^2$. 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 into Eq. (216) gives

$$pV = \frac{2}{3}N\langle \varepsilon_{\text{tr}} \rangle = \frac{2}{3}E_{\text{tr}}. \tag{217}$$

Let me assert that temperature, T, is a monotonic function of E_{tr}. Then if T is constant, E_{tr} is constant, so that P is proportional to $1/V$. This is a first-principles derivation of Boyle's Law.

What is the relation between T and E_{tr}? Let us compare with the ideal gas law:

$$PV = nRT = NkT = \frac{2}{3}E_{\text{tr}} \tag{218}$$

$$E_{\text{tr}} = \frac{3}{2}NkT = \frac{3}{2}nRT \tag{219}$$

that is, T is linear in E_{tr}, and the proportionality constant is $\frac{3}{2}R$ times the number of moles of molecules.

The average *squared* speed is c^2, so the "root-mean-square speed", c, comes from

$$\langle \varepsilon_{\text{tr}} \rangle = \frac{1}{2}mc^2 = \frac{3}{2}kT \tag{220}$$

$$c^2 = \frac{3kT}{m} \tag{221}$$

$$c = \left(c^2\right)^{\frac{1}{2}} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} \tag{222}$$

Notice in the last equation, I have written the formula both in terms of k and the molecular mass, and then in terms of the gas constant R and the molar mass (which must be in kg, not in g!) Using the last form in problems can often save annoying conversions from amu to kg and lets you use the gas constant $R = 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$ rather than Boltzmann's constant.

9.3 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.

9.3.1 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

$$P(a \leq v_x \leq b) = \int_a^b f(v_x)\, dv_x \tag{223}$$

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

$$\int_{-\infty}^{\infty} f(v_x)\, dv_x = 1 \tag{224}$$

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:

$$\frac{dN_{v_x v_y v_z}}{N} = f(v_x)\,f(v_y)\,f(v_z)\,dv_x\,dv_y\,dv_z \tag{225}$$

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

$$f(v_x)\,f(v_y)\,f(v_z) = \phi(v) \tag{226}$$

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 is equal to a single function of the sum of the arguments? There's only one function that does that: the exponential, because $e^a e^b e^c = e^{a+b+c}$. So the candidate function is

$$f(v_x) = Ae^{-\frac{1}{2}bv_x^2}, \tag{227}$$

a Gaussian! I have inserted the $-\frac{1}{2}$ for later convenience (this causes no loss of generality). 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

$$\int_{-\infty}^{\infty} Ae^{-\frac{1}{2}bv_x^2}\,dv_x = 1 \tag{228}$$

We can do this using the standard integral

$$\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}, \tag{229}$$

where $a > 0$, so that

$$A\left(\frac{2\pi}{b}\right)^{\frac{1}{2}} = 1 \tag{230}$$

$$A = \left(\frac{b}{2\pi}\right)^{\frac{1}{2}} \tag{231}$$

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 $c^2 = 3\langle v_x^2\rangle = \frac{3kT}{m}$, so that $\langle v_x^2\rangle = \frac{kT}{m}$. We can also calculate that average from the probability density function, using the usual formula for the average of a function:

$$\langle v_x^2\rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)\, dv_x \tag{232}$$

$$= \left(\frac{b}{2\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} v_x^2 e^{-\frac{1}{2}bv_x^2}\, dv_x \tag{233}$$

We need the standard integral

$$\int_{-\infty}^{\infty} x^{2n} e^{-ax^2}\, dx = \frac{(2n)!\,\pi^{\frac{1}{2}}}{2^{2n} n! a^{n+1/2}}, \tag{234}$$

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

$$\langle v_x^2\rangle = \left(\frac{b}{2\pi}\right)^{\frac{1}{2}} \frac{2!\,\pi^{\frac{1}{2}}}{2^2 (b/2)^{3/2}} \tag{235}$$

$$= \frac{1}{b} \tag{236}$$

so we now have

$$b = (\langle v_x^2\rangle)^{-1} \tag{237}$$

$$= \left(\frac{kT}{m}\right)^{-1} \tag{238}$$

$$= \frac{m}{kT} \tag{239}$$

so that finally

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{mv_x^2}{2kT}\right). \tag{240}$$

This expression gives us the one-dimensional distribution of velocity. Examples are plotted in Figure 14.

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.)

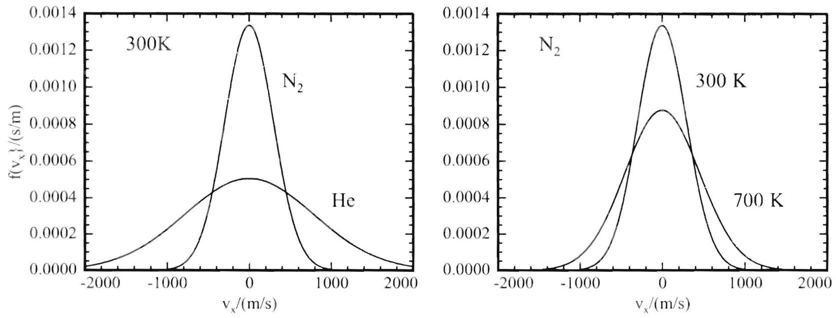

Figure 14: The one-dimensional velocity distribution, showing variations with molecular mass and with temperature. The area under each curve is 1.

Notice that the one-dimensional distribution can be written

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{\varepsilon_{\mathrm{tr}}}{kT}\right). \tag{241}$$

The exponential term is the ratio of two terms, each with dimensions of energy: the "one-dimensional translational energy" of the molecule, $\varepsilon_{\mathrm{tr}}$, 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.

9.3.2 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. (Atkins (pp. 26–27) calls this function $f(v)$; I will call it $F(v)$ to make a clearer distinction between it and the one-dimensional distribution of velocity components, $f(v_x)$.)

Eq. (225) 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,

$$\frac{dN_{v_x v_y v_z}}{N} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right) dv_x\, dv_y\, dv_z \tag{242}$$

(Notice that the exponent on the normalization factor is now $\frac{3}{2}$.) If you think of the function $\frac{dN_{v_x v_y v_z}}{N}$ 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. (242) describes the volume of a small rectangular box, which is located a distance v from the origin. Since we are looking for a distribution in speed only, and we don't care what direction the molecule is moving, we must add up all the probabilities like that one that correspond to the same total speed, v. All the little boxes that correspond to the same speed form a thin spherical shell of thickness dv a distance v from the origin. The total volume of such a shell is $4\pi v^2\, dv$, so to get our 3D *speed* distribution we must replace $dv_x\, dv_y\, dv_z$ with $4\pi v^2\, dv$, and replace $v_x^2 + v_y^2 + v_z^2$ with v^2. (You can reach this conclusion more rigorously by changing Eq. (242) to spherical polar coordinates, then integrating over the angular coordinates θ and ϕ.) So our final distribution of molecular speeds is

$$F(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 \exp\left(-\frac{mv^2}{2kT}\right) \tag{243}$$

Eq. (243) 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 15 shows examples corresponding to the 1D distributions we saw before.

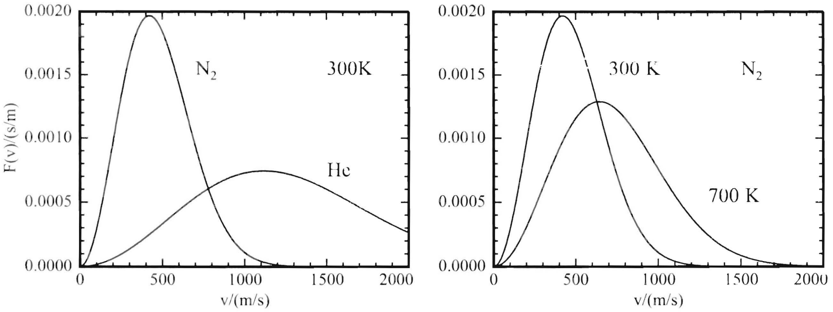

Figure 15: The Maxwell distribution of speeds. The area under each of the curves is 1.

10 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", as described briefly in Atkins on p. 29, 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).

In Doppler spectroscopy, the absorption spectrum of gas molecules is measured with very high resolution. Nowadays such spectroscopy is always 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.

10.1 Applications of the Maxwell distribution

10.1.1 Average speed $\langle v\rangle$

We use the usual approach to averaging things:

$$\langle v\rangle = \int_0^\infty vF(v)\,dv \tag{244}$$

$$= \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2kT}\right)\,dv \tag{245}$$

Use the standard integral

$$\int_0^\infty x^{2n+1} e^{-ax^2}\,dx = \frac{n!}{2a^{2n+1}} \tag{246}$$

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

$$\langle v\rangle = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi \frac{1!}{2\left(\frac{m}{2kT}\right)^2} \tag{247}$$

$$= \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} \tag{248}$$

The average speed $\langle v\rangle$ differs from the root-mean-square speed $\sqrt{\langle v^2\rangle}$ because it contains the numerical factor $\sqrt{8/\pi} = \sqrt{2.546}$ rather than $\sqrt{3}$. Atkins (section 1.3) gives $\langle v\rangle$ the symbol $\bar{c}$.

10.1.2 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}:

$$\frac{dF(v)}{dv} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi \left[2v + v^2\left(\frac{-mv}{kT}\right)\right] \exp\left(-\frac{mv^2}{2kT}\right) \tag{249}$$

$$0 = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi \left[2v_{\mathrm{mp}} + v_{\mathrm{mp}}^2\left(\frac{-mv_{\mathrm{mp}}}{kT}\right)\right] \exp\left(-\frac{mv_{\mathrm{mp}}^2}{2kT}\right) \tag{250}$$

Lots of stuff divides out, leaving

$$0 = \left[2v_{\mathrm{mp}} + v_{\mathrm{mp}}^2\left(\frac{-mv_{\mathrm{mp}}}{kT}\right)\right] \tag{251}$$

$$0 = 2 - \frac{mv_{\mathrm{mp}}^2}{kT} \tag{252}$$

$$v_{\mathrm{mp}} = \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \tag{253}$$

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.

10.2 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. However, we must be careful: we have to 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 $G(\varepsilon_{\mathrm{tr}})$, we must have $G(\varepsilon_{\mathrm{tr}})\,d\varepsilon_{\mathrm{tr}} = F(v)\,dv$. Therefore, we must be careful to change variables in the accompanying differential dv as well as in $F(v)$ itself.

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

$$G(\varepsilon_{\mathrm{tr}})\,d\varepsilon_{\mathrm{tr}} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi\left(\frac{2\varepsilon_{\mathrm{tr}}}{m}\right)\exp\left(-\frac{\varepsilon_{\mathrm{tr}}}{kT}\right)\left(\frac{1}{2m}\right)^{\frac{1}{2}}\varepsilon_{\mathrm{tr}}^{-\frac{1}{2}}d\varepsilon_{\mathrm{tr}} \tag{254}$$

$$= 2\pi\left(\frac{1}{\pi kT}\right)^{\frac{3}{2}}\varepsilon_{\mathrm{tr}}^{\frac{1}{2}}\exp\left(-\frac{\varepsilon_{\mathrm{tr}}}{kT}\right)\,d\varepsilon_{\mathrm{tr}} \tag{255}$$

All the dependence on mass has canceled; the translational energy distribution is the same for all molecules at the same temperature. Figure 16 shows this distribution for temperatures of 300 and 700 K.

The translational energy distribution rises very steeply from the origin; it has infinite slope at the origin, while the speed distribution has zero slope

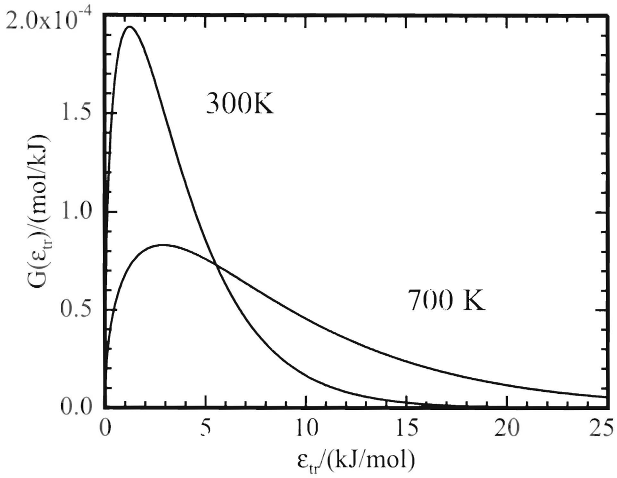

Figure 16: Translational energy distributions for gases. The distribution is independent of mass.

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 than can surmount an "activation barrier" and react; this distribution therefore plays an important role in kinetics.

10.3 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 17.) In a time t, our molecule carves out a "collision cylinder" of volume $\pi d^2 v_{\mathrm{rel}} t$; 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

$$z = \pi d^2 v_{\mathrm{rel}} \mathcal{N}. \tag{256}$$

Figure 17: The collision cylinder; cf. Figure 1.20 in Atkins.

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

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{PN_A}{RT} = \frac{P}{kT} \tag{257}$$

so that in terms of the pressure the collision rate is

$$z = \pi d^2 v_{\mathrm{rel}} \frac{P}{kT} \tag{258}$$

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:

$$v_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \tag{259}$$

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. (258).

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

$$Z_{AB} = z_{AB}\mathcal{N}_A \tag{260}$$

$$Z_{AB} = \sigma_{AB}\left(\frac{8kT}{\pi\mu_{AB}}\right)^{\frac{1}{2}}\left(\frac{P_A}{kT}\right)\left(\frac{P_B}{kT}\right). \tag{261}$$

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:

$$Z_{BB} = \frac{1}{2} z_{BB}\mathcal{N}_B \tag{262}$$

$$Z_{BB} = \frac{1}{2}\sigma_{BB}\left(\frac{8kT}{\pi\mu_{BB}}\right)^{\frac{1}{2}}\left(\frac{P_B}{kT}\right)^2 \tag{263}$$

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

10.3.1 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:

$$\lambda = \langle v\rangle/z = \frac{kT}{\sqrt{2}\sigma P} \tag{264}$$

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

11 Real gases

11.1 $p - V$ 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 18 for an illustration.

Figure 18: The P-V isotherm for a pure gas 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. But here's something you might not have expected: the liquification sets in 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 19 to see the qualitative behavior of the isotherms. Atkins gives an accurate set of isotherms for CO_2 in Figure 1.23 on page 31.

Figure 19: Isotherms of a pure substance. Successively higher lines occur at higher temperatures.

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 followed 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.

11.2 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

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \tag{265}$$

The numbers a and b are different for each gas; a, which must have units (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 $-a\left(\frac{n}{V}\right)^2$, which reduces the pressure, gets smaller as the density decreases, as you expect.

Table 1.6 in the Data section of Atkins gives van der Waals constants a and b for about twenty gases. They can also be estimated from the critical temperature and pressure:

$$a = \frac{27R^2T_c^2}{64p_c}. \tag{266}$$

$$b = \frac{RT_c}{8p_c}. \tag{267}$$

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 cm^3/mol, while the molar volume of liquid water is 18 cm^3/mol. b for benzene is 115 cm^3/mol; the molar volume of liquid benzene is 89 cm^3/mol.

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

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{268}$$

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 $p = RT/V_m$.

11.2.1 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 19 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 20 shows isotherms calculated from the van der Waals equation using the constants for CO_2 ($a = 3.640\,\text{atm}\,\text{L}^2\,\text{mol}^{-2}$, $b = 0.04267\,\text{L}\,\text{mol}^{-1}$.) 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. (Atkins describes this trick on page 36.) As temperature increases, the loops diminish in amplitude, until finally they disappear; at one particular temperature, the curve has a slope of zero exactly at one molar volume, and negative slope everywhere else. This gives an isotherm that looks like the critical isotherm; it occurs at a temperature of $T_c^{\text{vdw}} = \frac{8a}{37bR}$, which with the van der Waals constants for CO_2 comes out to be 307.9 K. The experimental critical temperature T_c is 304.1282 K. At temperatures above T_c the van der Waals isotherms qualitatively resemble the experimental ones.

11.2.2 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; some use more parameters in hopes of higher accuracy at the cost of more complication; and one, the *virial equation of state*, replaces the

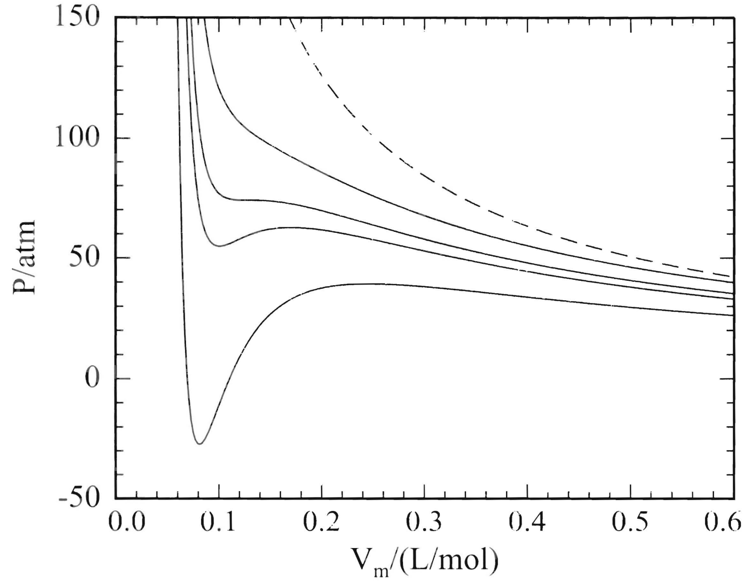

Figure 20: Isotherms for CO_2 from the van der Waals equation. From the bottom, the curves represent isotherms at 246.3, 292.5, 307.9, and 338.7 K, which represent, respectively, 0.8, 0.95, 1.0, and 1.1 times T_c^{vdw}. The dashed line gives the ideal gas isotherm at 307.9 K.

constants for each gas with functions of temperature, giving an effectively infinite number of adjustable paramters. We will consider two of these.

11.3 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

$$p = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}(V_{\mathrm{m}} + b)T^{1/2}} \tag{269}$$

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

$$a = \frac{R^2 T_c^{5/2}}{9p_c(2^{1/3} - 1)} \tag{270}$$

$$b = \frac{(2^{1/3} - 1)RT_c}{3p_c} \tag{271}$$

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.

Atkins, in Table 1.7, shows several other equations of state. Many more (hundreds!) 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.

11.4 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

$$pV_m = RT\left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \cdots\right) \tag{272}$$

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 betwen 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

$$B(T) = -2\pi N_A \int_0^\infty \left(\exp\left(\frac{-v(r)}{kT}\right) - 1\right) r^2 \, dr \tag{273}$$

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. (273) 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.)

12 First Law of thermodynamics

We already calculated the average kinetic energy of the particles in an ideal gas: $\langle \varepsilon_{\text{tr}} \rangle = \frac{3}{2}kT$. 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 any thing 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 exactly in half (by putting a partition in the container, for example), each half has exactly 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 conduct heat, 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), 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, there will be no more heat flow.

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 piston-and-cylinder 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 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 (ideal gas or otherwise) during any process is equal to the sum of the heat flow into the system, q, and the work done on the system, w:

$$\Delta E = q + w \tag{274}$$

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

$$\Delta U = q + w \tag{275}$$

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, is so deeply ingrained into our language that it was impossible for me to avoid saying "a container whose walls conduct heat" above. The idea of heat-as-fluid also persists in terms like "heat capacity" and "heat flow".

(Incidentally, an early serious attack on the caloric theory was made 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.)

12.1 Example: 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 atmospheres 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 mass of the plunger is 10 g.

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?

Solving this problem requires two insights: first, that since the gas ends at the same temperature as it began, its internal energy is unchanged ($\Delta U = 0$), and second, that the force against which it is pushing is constant, so that 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 plus the weight of the plunger, that is,

$$F_{\text{ext}} = p_{\text{ext}} A + mg, \tag{276}$$

where p_{ext} is the external atmospheric pressure, A is the area of the plunger face, m is the mass of the plunger, and g is the acceleration of gravity. Plugging in the values and changing units appropriately, we find $F_{\text{ext}} = 40.1\text{ N}$, so that $w = F\Delta x = (40.1\text{ N})(-0.02\text{ m}) = -0.802\text{ J}$. 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 and is adopted by Atkins.

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.

12.2 General pV work

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

$$dw = -p_{\text{ext}} A\, dx = -p_{\text{ext}}\, dV \tag{277}$$

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

$$dw = -p_{\text{ext}}\, dV. \tag{278}$$

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.

12.2.1 Expansion against constant external pressure

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

$$w = -\int_{V_1}^{V_2} p_{\text{ext}} dV = -p_{\text{ext}} \int_{V_1}^{V_2} dV = -p_{\text{ext}}(V_2 - V_1) = -p_{\text{ext}}\Delta V. \tag{279}$$

Figure 21: 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.

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,

$$w = -\int_{V_1}^{V_2} p_{\text{ext}}(V)dV, \tag{280}$$

and the work is the area under the curve $p_{\text{ext}}(V)$ on a $p - V$ diagram. Notice (Figure 21) 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.

12.2.2 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.

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

$$w = -\int_{V_1}^{V_2} p_{\text{ext}}(V)\,dV \tag{281}$$

Since the expansion is reversible we replace p_{ext} with p:

$$= -\int_{V_1}^{V_2} p(V)\,dV \tag{282}$$

$$= -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV \tag{283}$$

$$= -nRT\int_{V_1}^{V_2} \frac{dV}{V} \tag{284}$$

$$= -nRT\,[\ln V]_{V_1}^{V_2} \tag{285}$$

$$= -nRT\ln\left(\frac{V_2}{V_1}\right) \tag{286}$$

12.3 Enthalpy

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

$$\Delta U = U_2 - U_1 = q_V \tag{287}$$

(where the subscript V indicates constant volume.)

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

$$\Delta U = U_2 - U_1 = q_p + w_p = q_p - p(V_2 - V_1), \tag{288}$$

so that

$$(U_2 + pV_2) - (U_1 + pV_1) = q_p \tag{289}$$

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

$$H = U + pV \tag{290}$$

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

$$H_2 - H_1 = \Delta H = q_p \tag{291}$$

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.

12.4 Heat capacities

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

$$dq = C\,dT \tag{292}$$

or

$$C = \frac{dq}{dT} \tag{293}$$

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

$$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \tag{294}$$

$$C_p = \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p \tag{295}$$

$C_p \geq C_V$ 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. 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. It also applies to entire systems; 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 1 g or 1 kg of a specified substance by 1 K (typically at constant pressure). The other is the *molar heat capacity*, $C_{V,\mathrm{m}}$ or $C_{p,\mathrm{m}}$, which is the heat capacity per mole of substance.

12.4.1 Heat capacities for ideal gases

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

Differentiating with respect to T at constant p gives

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{296}$$

and from the ideal gas law we can evaluate the last term to give

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\frac{nR}{p} \tag{297}$$

For an ideal gas, U and H are both functions of T alone; neither depends on V or p (since the product pV is constant). Therefore for an ideal gas

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p = \frac{dU}{dT} \tag{298}$$

We therefore have

$$\left(\frac{\partial H}{\partial T}\right)_p = C_V + p\frac{nR}{p} \tag{299}$$

$$C_p = C_V + nR \tag{300}$$

Thermodynamics does not give us theoretical tools to predict heat capacities; they are quantities that must be measured for each substance. 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

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR. \tag{301}$$

The heat capacity at constant pressure is therefore

$$C_p = C_V + nR = \frac{5}{2}nR. \tag{302}$$

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

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}nR}{\frac{3}{2}nR} = \frac{5}{3}. \tag{303}$$

This value is observable experimentally and is accurately 1.667 for noble gases at low densities.

12.4.2 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:

$$dw = -p\,dV = -\frac{nRT}{V}dv \tag{304}$$

$$dw = dU = C_V dT \tag{305}$$

Equating those two and dividing by T separates the variables:

$$C_V\frac{dT}{T} = -nR\frac{dV}{V} \tag{306}$$

Integrate both sides:

$$\int_{T_1}^{T_2} C_V\frac{dT}{T} = -nR\int_{V_1}^{V_2}\frac{dV}{V} \tag{307}$$

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

$$C_V \ln\left(\frac{T_2}{T_1}\right) = -nR\ln\left(\frac{V_2}{V_1}\right). \tag{308}$$

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. (308) to get

$$C_V \ln\left(\frac{T_2}{T_1}\right) = -(C_p - C_V)\ln\left(\frac{V_2}{V_1}\right) \tag{309}$$

and writing $C_p/C_V = \gamma$ gives

$$\ln\left(\frac{T_2}{T_1}\right) = (1-\gamma)\ln\left(\frac{V_2}{V_1}\right) \tag{310}$$

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,

$$\frac{V_2}{V_1} = \frac{T_2}{p_2}\frac{p_1}{T_1} \tag{311}$$

and substituting for the ratio of volumes gives

$$\ln\left(\frac{T_2}{T_1}\right) = (1-\gamma)\ln\left(\frac{T_2 p_1}{T_1 p_2}\right). \tag{312}$$

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

$$\frac{T_2}{T_1} = \left(\frac{T_2 p_1}{T_1 p_2}\right)^{1-\gamma} = \left(\frac{T_1 p_2}{T_2 p_1}\right)^{\gamma-1}, \tag{313}$$

and we can gather terms to get

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{p_2}{p_1}\right)^{\gamma-1} \tag{314}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}. \tag{315}$$

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

$$\frac{T_2}{T_1} = \left(\frac{10^{-2}}{2000}\right)^{\frac{2/3}{5/3}} = (5 \times 10^{-6})^{2/5} = 0.0076, \tag{316}$$

so that the final temperature is 2.3 K! This experiment can be carried out in an apparatus that uses a medium-size diffusion pump (20 cm 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.

12.5 Standard enthalpy changes

12.5.1 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 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 which 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 tablulated 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 under which the reaction occurs. The temperature is generally specified explicitly; most enthalpies of formation are given at 298.15 K, but values are sometimes availble at other temperatures. For many years the standard pressure was 1 atm, but recently the standard has been changing to 1 bar.

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

$$3\mathrm{C(s)} + 3\mathrm{H_2(g)} \longrightarrow \mathrm{C_3H_6(g)} \tag{317}$$

is carried out at 1 bar pressure and 298.15 K. The symbol for this quantity is $\Delta_\mathrm{f} H^\ominus_{298.15}$. 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 $^\ominus$ indicates "standard state", which is some agreed-upon set of conditions which taken together with the temperature is sufficient to 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 discouraged) 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:

$$\begin{array}{rcll}
\mathrm{C_3H_6}(g)(\text{cyclopropane}) & \longrightarrow & 3\mathrm{C}(s) + 3\mathrm{H_2}(g) & (318)\\
3\mathrm{C}(s) + 3\mathrm{H_2}(g) & \longrightarrow & \mathrm{C_3H_6}(g)(\text{propene}) & (319)\\
\hline
\mathrm{C_3H_6}(g)(\text{cyclopropane}) & \longrightarrow & \mathrm{C_3H_6}(g)(\text{propene}) & (320)
\end{array}$$

Eq. (319) 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. (318) 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. (318) 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.

12.5.2 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 occuring 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

$$\Delta H = \int_{350}^{298.15} C_p^{\mathrm{c}}\, dT \tag{321}$$

   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 $\Delta_{\mathrm{r}} H^{\ominus} = -32.9$ kJ/mol.

3. Heat propene from 298.15 to 350 K. The enthalpy change for that process is

$$\Delta H = \int_{298.15}^{350} C_p^{\mathrm{p}}\, dT \tag{322}$$

   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; it is plotted in Figure 22.

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:

$$\Delta H = \int_{350}^{298.15} C_p^{\mathrm{c}}\, dT + \Delta_{\mathrm{r}} H^{\ominus}_{298.15} + \int_{298.15}^{350} C_p^{\mathrm{p}}\, dT \tag{323}$$

$$= \Delta_{\mathrm{r}} H^{\ominus}_{298.15} + \int_{298.15}^{350} C_p^{\mathrm{p}} - C_p^{\mathrm{c}}\, dT \tag{324}$$

$$= \Delta_{\mathrm{r}} H^{\ominus}_{298.15} + \int_{298.15}^{350} \Delta C_p\, dT \tag{325}$$

Table 4 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

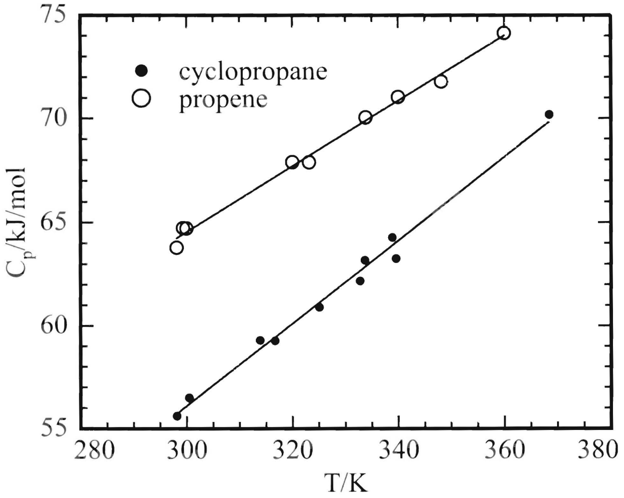

Figure 22: Heat capacity data from Table 4. Lines are fitted through both sets; for cyclopropane, the slope is 0.200 J/mol K and the intercept is −4.16 J/mol, while for propene the slope is 0.158 J/mol K and the intercept is 17.19 J/mol.

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

$$\Delta H = \Delta_{\mathrm{r}} H^{\ominus}_{298.15} + \int_{298.15}^{350} \Delta C_p \, dT \tag{326}$$

$$= \Delta_{\mathrm{r}} H^{\ominus}_{298.15} + \int_{298.15}^{350} (c - a) + (d - b)T \, dT \tag{327}$$

$$= \Delta_{\mathrm{r}} H^{\ominus}_{298.15} + \Big[(c - a)T + (d - b)T^2\Big]_{298.15}^{350} \tag{328}$$

$$= \Delta_{\mathrm{r}} H^{\ominus}_{298.15} + \Big[(17.19 - (-4.16))T + (.158 - .200)T^2\Big]_{298.15}^{350} \tag{329}$$

$$= -32.9\,\mathrm{kJ/mol} - 304\,\mathrm{J/mol} \tag{330}$$

$$= -33.2\,\mathrm{kJ/mol} \tag{331}$$

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 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 $\Delta_{\mathrm{fus}} H$ or $\Delta_{\mathrm{vap}} H$) 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.

12.6 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, $\Delta_{\mathrm{fus}} H$ and $\Delta_{\mathrm{vap}} H$; for sublimation there is also a $\Delta_{\mathrm{sub}} H$. In all cases, these values give the amount of heat absorbed by one mole of the substance while it undergoing 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 $\Delta_{\mathrm{sub}} H^{\ominus}$ 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.

13 Mathematical interlude

13.1 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 the section called *Further Information I* near the back of Atkins.

13.1.1 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:

$$\left(\frac{\partial f}{\partial z}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x \tag{332}$$

For example,

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial V_\mathrm{m}}\right)_T \left(\frac{\partial V_\mathrm{m}}{\partial V}\right)_T = \frac{1}{n}\left(\frac{\partial p}{\partial V_\mathrm{m}}\right)_T. \tag{333}$$

13.1.2 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:)

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z} \tag{334}$$

This property is often very handy when you work with real gases. The van der Waals equation is difficult to write in the form $V_\mathrm{m} = f(p, T)$, 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:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{335}$$

$$= -\frac{1}{V}\frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} \tag{336}$$

The van der Waals equation is most conveniently written in terms of V_{m}, so apply the chain rule:

$$= -\frac{1}{V}\frac{1}{\left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T \left(\frac{\partial V_{\mathrm{m}}}{\partial V}\right)_T} \tag{337}$$

$$= -\frac{1}{V}\frac{1}{\left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T \frac{1}{n}} \tag{338}$$

$$= -\frac{1}{V_{\mathrm{m}}}\frac{1}{\left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T} \tag{339}$$

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

$$\kappa_T = \frac{V_{\mathrm{m}}^2 (V_{\mathrm{m}} - b)^2}{RTV_{\mathrm{m}}^3 - 2a(V_{\mathrm{m}} - b)^2} \tag{340}$$

13.1.3 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:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \tag{341}$$

13.1.4 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.

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \tag{342}$$

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

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H . \tag{343}$$

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

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T . \tag{344}$$

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

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \tag{345}$$

$$= -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T \tag{346}$$

$$= -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \tag{347}$$

$$= -\frac{\mu_T}{C_p} \tag{348}$$

13.2 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

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{349}$$

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

$$dz = f(x, y)dx + g(x, y)dy, \tag{350}$$

then the differential dz is exact if and only if

$$\left(\frac{\partial f(x,y)}{\partial y}\right)_x = \left(\frac{\partial g(x,y)}{\partial x}\right)_y . \tag{351}$$

Here's a trivial example. Consider the internal energy change during an expansion of an ideal gas. We can rewrite Eq. (349) as

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{352}$$

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

$$dU = C_V dT + 0\, dV \tag{353}$$

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

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial 0}{\partial T}\right)_V \tag{354}$$

On the left, we have

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T \tag{355}$$

The order of partial differentiation does not matter, so

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V \tag{356}$$

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.)

14 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

$$dq = dU - dw = C_V\, dT - p\, dV \tag{357}$$

For this to be exact, we would have to have

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial C_V}{\partial V}\right)_T. \tag{358}$$

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

$$\frac{dq}{T} = \frac{C_V}{T}dT - \frac{p}{T}dV \tag{359}$$

and the Euler criterion is

$$\left(\frac{\partial(C_V/T)}{\partial V}\right)_T = \left(\frac{\partial(p/T)}{\partial T}\right)_V \tag{360}$$

$$\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial(nR/V)}{\partial T}\right)_V \tag{361}$$

$$0 = 0 \tag{362}$$

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.

15 The Second Law

15.1 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 tht 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.

15.2 Existence of the entropy

Figure 23: A cycle in the T, V plane. Section $1 \rightarrow 2$ is a reversible adiabat; section $2 \rightarrow 3$ is a reversible isotherm.

Figure 23 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 $1 \to 2$ is a reversible adiabat; adiabatic means $q_{1\to 2} = 0$. The path $2 \to 3$ is a reversible isothermal expansion; such an expansion requires $q_{2\to 3} > 0$. Finally, the path $3 \to 1$ is a reversible adiabat with $q_{3\to 1} = 0$. 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 Law. There is no reversible adiabat connecting points 2 and 3.

This argument holds for any substance and any isothermal path $2 \to 3$, 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, $f(T, V) =$ 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.

To proceed further, I consider what happens when we "step off" one of the reversible adiabats; that is, I consider the change in S brought about by a reversible heat flow. I must have

$$dS(T, V) = \Theta(T, V)\, dq_{\mathrm{rev}} \tag{363}$$

where $\Theta(T, V)$ is some as-yet-unknown function of T and V. For reversible adiabatic processes, $dq_{\mathrm{rev}} = 0$ and this expression reduces to $dS(T, V) = 0$ as it must.

dq_{rev} depends on the path of the reversible heat transfer; on the other hand, because the reversible adiabats are unique, $S(T, V)$ must be a state function so $dS(T, V)$ must be an exact differential. The function $\Theta(T, V)$ therefore plays a special role; in differential equations it is called an *integrating factor.*

Consider two samples of material contained in an adiabatic can, both at temperature T but with different volumes V_1 and V_2. If a small amount of heat dq_{rev} is transferred reversibly between them, then $dq_1 = -dq_2$. Because there is no heat flow from the overall surroundings, the entropy of the overall system does not change, and $dS = dS_1 + dS_2 = 0$. Then from

Eq. (363) we have

$$[\Theta_1(T, V_1) - \Theta_2(T, V_2)]dq_1 = 0. \tag{364}$$

Since this is true no matter what V_1 and V_2 are, and $dq_1 \neq 0$, we conclude that

$$\Theta_1(T, V_1) = \Theta_2(T, V_2) = \Theta(T), \tag{365}$$

that is, the function $\Theta(T, V)$ does not depend on the volume but only on the temperature, and can be written simply $\Theta(T)$. Furthermore, none of the arguments we have made so far have dependended on the properties of any substance; $\Theta(T)$ must be universal, that is, the same function $\Theta(T)$ must apply to all substances. If we can figure out what it is for any substance, we will have the formula for every substance. Let's use the easiest substance to work with, the ideal gas.

For the ideal gas we have

$$pV = nRT \tag{366}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{367}$$

The First Law gives us for a reversible change

$$dU = dq + dw = dq - pdV \tag{368}$$

but for the ideal gas we have

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{369}$$

$$= C_V\, dT \tag{370}$$

(because $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas.) Then

$$dq = C_V\, dT + \frac{nRT}{V}\, dV \tag{371}$$

Substituting into Eq. (363) I find

$$dS = \Theta(T)dq = \Theta(T)C_V(T)\, dT + \Theta(T)\frac{nRT}{V}\, dV \tag{372}$$

We know from the uniqueness of reversible adiabats that $S(T, V)$ is a state function, so dS must be an exact differential. The Euler criterion then tells us

$$\left[\frac{\partial}{\partial V}(\Theta(T)C_V(T))\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\Theta(T)nRT}{V}\right)\right]_V \tag{373}$$

For the ideal gas,

$$\left[\frac{\partial}{\partial V}(\Theta(T)C_V(T))\right]_T = \Theta(T)\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \tag{374}$$

because C_V is a function of temperature but not volume for an ideal gas. Therefore,

$$\left[\frac{\partial}{\partial T}\left(\frac{\Theta(T)nRT}{V}\right)\right]_V = \frac{nR}{V}\frac{\partial}{\partial T}[T\Theta(T)]_V = 0, \tag{375}$$

and since $\frac{nR}{V} \neq 0$ we conclude that

$$\frac{\partial}{\partial T}[T\Theta(T)]_V = 0, \tag{376}$$

or that $T\Theta(T)$ is a constant. Any old constant will do; for reasons of convenience and consistency we choose to make $T\Theta(T) = 1$, or $\Theta(T) = 1/T$, so that

$$dS = \frac{dq_{\text{rev}}}{T}. \tag{377}$$

For any change,

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}. \tag{378}$$

The formula for dS involves the heat transfer in a *reversible* process. If the process you are interested in is not reversible (which is most processes), then to calculate ΔS you must fine 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. A simple example of such a calculation is Exercise 4.11 in your homework, which asks you to calculate the entropy change when two volumes of water at different temperatures are mixed together.

16 Examples of entropy calculations

16.1 Reversible isothermal expansion of ideal gas

In an isothermal change, T is constant, and for an ideal gas then U is also constant so $dq_{\text{rev}} = -dw = pdV$; then

$$dS = \frac{dq_{\text{rev}}}{T} \tag{379}$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{p}{T}\, dV \tag{380}$$

$$= \int_{V_1}^{V_2} \frac{nR}{V}\, dV \tag{381}$$

$$= nR \ln\left(\frac{V_2}{V_1}\right). \tag{382}$$

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

This procedure is typical of entropy calculations for reversible processes; you must figure out an expression for dq_{rev}, then integrate it over the process.

16.2 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 (and you do, in your homework, for a more complicated case) 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

$$dS = \frac{dq_{\text{rev}}}{T} = C_p \frac{dT}{T} \tag{383}$$

$$\Delta S_{\text{A}} = \int_{T_{\text{A}}}^{T_f} C_p \frac{dT}{T} \tag{384}$$

$$= C_p \ln\left(\frac{T_f}{T_{\text{A}}}\right) \tag{385}$$

Similarly, for sample B we find

$$\Delta S_{\text{B}} = C_p \ln\left(\frac{T_f}{T_{\text{B}}}\right) \tag{386}$$

so the total entropy change in the sample is

$$\Delta S = C_p \left[\ln\left(\frac{T_f}{T_{\text{A}}}\right) + \ln\left(\frac{T_f}{T_{\text{B}}}\right)\right]. \tag{387}$$

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".

16.3 Entropy changes in the surroundings

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

$$dH_{\text{surr}} = dq_{\text{surr}}, \tag{388}$$

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,

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T}. \tag{389}$$

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

$$\Delta S_{\text{surr}} = \frac{\Delta U_{\text{surr}}}{T}. \tag{390}$$

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 Helmholz energies.

16.4 Irreversible processes: the Clausius inequality

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

$$\Delta S = C_p \left[\ln\left(\frac{T_f}{T_{\text{A}}}\right) + \ln\left(\frac{T_f}{T_{\text{B}}}\right)\right], \tag{391}$$

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:

$$\begin{aligned}
\Delta S &= C_p \left[\ln\left(\frac{T_f}{T_{\text{A}}}\right) + \ln\left(\frac{T_f}{T_{\text{B}}}\right)\right] && (392)\\
&= C_p \left[\ln\left(\frac{T_f}{T_{\text{A}}}\frac{T_f}{T_{\text{B}}}\right)\right] && (393)\\
& && (394)
\end{aligned}$$

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

$$\begin{aligned}
\frac{T_f}{T_{\text{A}}}\frac{T_f}{T_{\text{B}}} &= \frac{\left(\frac{T_{\text{A}}+T_{\text{B}}}{2}\right)^2}{T_{\text{A}}T_{\text{B}}} && (395)\\
&= \frac{T_{\text{A}}^2 + 2T_{\text{A}}T_{\text{B}} + T_{\text{B}}^2}{4T_{\text{A}}T_{\text{B}}} && (396)\\
&= \frac{1}{2} + \frac{T_{\text{A}}^2 + T_{\text{B}}^2}{4T_{\text{A}}T_{\text{B}}} && (397)\\
&= \frac{1}{2} + \frac{1}{4}\left(\frac{T_{\text{A}}}{T_{\text{B}}} + \frac{T_{\text{B}}}{T_{\text{A}}}\right) && (398)
\end{aligned}$$

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

$$\frac{1}{2}+\frac{1}{4}\left(\frac{T_\mathrm{A}}{T_\mathrm{B}}+\frac{T_\mathrm{B}}{T_\mathrm{A}}\right) > 1 \tag{399}$$

$$\frac{T_\mathrm{A}}{T_\mathrm{B}}+\frac{T_\mathrm{B}}{T_\mathrm{A}} > 2 \tag{400}$$

$$\left(\frac{T_\mathrm{A}}{T_\mathrm{B}}\right)^2+1 > 2\frac{T_\mathrm{A}}{T_\mathrm{B}} \tag{401}$$

$$\left(\frac{T_\mathrm{A}}{T_\mathrm{B}}-1\right)^2 > 0 \tag{402}$$

which will be true for any $T_\mathrm{A} \neq T_\mathrm{B}$. 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.

17 Gibbs and Helmholtz energies

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, then we must have, for any small spontaneous change,

$$dS_{\text{sys}} + dS_{\text{surr}} > 0. \tag{403}$$

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

$$dS_{\text{surr}} = -\frac{dH}{T} \tag{404}$$

leading to

$$dS_{\text{sys}} - \frac{dH}{T} > 0. \tag{405}$$

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

$$dH - TdS < 0. \tag{406}$$

(I have dropped the "sys" subscript.) 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

$$dU - TdS < 0. \tag{407}$$

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

$$G = H - TS \tag{408}$$

$$A = U - TS \tag{409}$$

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

$$dG < 0 \tag{410}$$

$$dA < 0 \tag{411}$$

Atkins has a good discussion at the bottom of page 114 that is worth reading. 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 is a misleading statement. 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. 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.

17.1 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

$$\frac{dq_{\text{rev}}}{T} + \frac{-dq}{T} \geq 0, \tag{412}$$

whence

$$dq_{\text{rev}} \geq dq, \tag{413}$$

or

$$dS \geq \frac{dq}{T}, \tag{414}$$

where all variables without subscripts apply to the system. In fact, Eq. (414) is sometimes called the Clausius inequality.

Atkins uses Eq. (414) to show by straightforward arguments (pages 114–117) that ΔA for a process gives the maximum amount of work that can be extracted from the process, and ΔG for a process gives the maximum amount of non-expansion work that can be extracted from the process. Along the way, in those arguments, he shows that any system does the maximum amount of work when it works reversibly. I shall not prove those things, but shall go on with similar arguments to move toward descriptions of equilibrium.

18 Alphabet soup: Maxwell relations and thermodynamic equations of state

We now move into Chapter 5 of Atkins and begin finding formulas that we can use to make predictions about chemistry.

The First Law gives

$$dU = dq + dw. \tag{415}$$

Restrict the discussion for a moment to reversible processes doing only expansion (pV) work. Then $dq = dq_{\text{rev}} = T\,dS$ and $dw = -p\,dV$ so we have

$$dU = T\,dS - p\,dV \tag{416}$$

Because U is a state function, dU is independent of whether the change is carried out reversibly or not. Therefore, this equation holds for any process doing only pV work. Atkins (but nobody else I know of) calls it the fundamental equation.

dU is an exact differential. We could have regarded U as a function of S and V and written immediately

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV. \tag{417}$$

Comparing Eq. (416) and Eq. (417) gives

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{418}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{419}$$

Also, because dU is an exact differential, the Euler criterion holds so that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_T \tag{420}$$

Eq. (420) 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 5 I list the results; you should be able to derive any expression in the later columns from the equation in the first.

Table 5 The Gibbs equations (first column), the resulting thermodynamic identities (second and third), and the corresponding Maxwell relations (last column).

$dU = T\,dS - p\,dV$	$\left(\frac{\partial U}{\partial S}\right)_V = T$	$\left(\frac{\partial U}{\partial V}\right)_S = -p$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$dH = T\,dS + V\,dp$	$\left(\frac{\partial H}{\partial S}\right)_p = T$	$\left(\frac{\partial H}{\partial p}\right)_S = V$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$dA = -S\,dT - p\,dV$	$\left(\frac{\partial A}{\partial T}\right)_V = -S$	$\left(\frac{\partial A}{\partial V}\right)_T = -p$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$
$dG = -S\,dT + V\,dp$	$\left(\frac{\partial G}{\partial T}\right)_p = -S$	$\left(\frac{\partial G}{\partial p}\right)_T = V$	$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

18.1 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 a student has already asked me about: "How do we know that $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_\mathrm{m}^2}$ 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:

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

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T . \tag{421}$$

In our table, we find simple expressions for two of those things:

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{422}$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{423}$$

giving

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial S}{\partial V}\right)_T. \tag{424}$$

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

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V. \tag{425}$$

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

$$p = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^2} \tag{426}$$

so that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_{\mathrm{m}} - b} \tag{427}$$

Substituting that into Eq. (425) gives

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + \frac{RT}{V_{\mathrm{m}} - b} = \frac{a}{V_{\mathrm{m}}^2} \tag{428}$$

after a simple substitution from the van der Waals equation.

19 The chemical potential

Our development so far has been for pure substances of constant composition. To make thermodynamics useful in chemistry we need to extend it to account for variable composition in a system, since chemically reacting systems are by definition changing in composition. We can therefore no longer regard our state functions G, S, and so on a 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 of constant composition,

$$dG = -S\,dT + V\,dp \tag{429}$$

That equation is a friendlier-looking version of

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp. \tag{430}$$

To add variables, 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

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_k} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_k} dp + \left(\frac{\partial G}{\partial n_k}\right)_{T,p} dn_k \tag{431}$$

If we have many different components, with numbers of moles of each one written as n_i, $i = 1, 2, 3 \ldots k$, then we write

$$\begin{aligned} dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_{i\neq 1}} dn_1 \\ + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_{i\neq 2}} dn_2 + \cdots + \left(\frac{\partial G}{\partial n_k}\right)_{T,p,n_{i\neq k}} dn_k \end{aligned} \tag{432}$$

which I can write as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} dn_i \tag{433}$$

We define the *chemical potential* of species i in a one-phase system (not necessarily at constant composition: this holds for different chemical species in a solution, for example) as

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{434}$$

The chemical potential tells how the Gibbs energy of a system changes when a substance is added to it.

Our Gibbs equation now returns to a friendlier-looking form:

$$dG = -S\,dT + V\,dp + \sum_{i=1}^{k} \mu_i\,dn_i \tag{435}$$

According to Levine: "(Eq. (435)) is the key equation in chemical thermodynamics." It applies to a closed 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.

19.1 Chemical potential of a pure substance

If there is only one component, then we have

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = \left(\frac{\partial nG_\mathrm{m}}{\partial n}\right)_{T,p} = G_\mathrm{m}, \tag{436}$$

that is, for a pure substance the chemical potential is simply the molar Gibbs energy.

19.1.1 Variation of chemical potential with pressure of ideal gas

We have for a one-component system

$$dG = -S\,dT + V\,dp$$

If we consider an isothermal change of pressure of an ideal gas, we find

$$\Delta G = \int_{p_1}^{p_2} V\,dp \tag{437}$$

$$= \int_{p_1}^{p_2} \frac{nRT}{p}\,dp \tag{438}$$

$$= nRT\ln\left(\frac{p_2}{p_1}\right) \tag{439}$$

Now if we define one particular pressure (traditionally one atmosphere, nowadays one bar) as the "standard pressure", then we can say

$$G(p) = G^{\ominus} + nRT\ln\left(\frac{p}{p^{\ominus}}\right) \tag{440}$$

Differentiating with respect to n, we find

$$\mu(p) = \mu^{\ominus} + RT\ln\left(\frac{p}{p^{\ominus}}\right) \tag{441}$$

This tells us, for a pure perfect gas, how the chemical potential varies with pressure.

19.2 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. (435) 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,

$$dG = -S\,dT + V\,dp + \sum_{\alpha=1}^{m}\sum_{i=1}^{k}\mu_i^{\alpha}\,dn_i^{\alpha} \tag{442}$$

where the superscript α denotes the phase.

20 Conditions for material equilibrium

In Section 17 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. (442) then reads

$$\sum_{\alpha=1}^{m}\sum_{i=1}^{k}\mu_i^{\alpha}\,dn_i^{\alpha} = 0. \tag{443}$$

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. (443). In fact, Eq. (443) 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. (443) 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 form 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.

20.1 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. (443) says that at equilibrium, the sum

$$\mu_{\mathrm{l}}\, dn_{\mathrm{l}} + \mu_{\mathrm{g}}\, dn_{\mathrm{g}} = 0, \tag{444}$$

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 $dn_{\mathrm{l}} = -dn_{\mathrm{g}}$. Substituting for dn_{l} and rearranging I find

$$(\mu_{\mathrm{g}} - \mu_{\mathrm{l}})\, dn_{\mathrm{g}} = 0 \tag{445}$$

or, dividing by dn_{g},

$$\mu_{\mathrm{g}} = \mu_{\mathrm{l}}. \tag{446}$$

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.

20.2 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

$$\mathrm{C_3H_6O_3} + 3\mathrm{O_2} \longrightarrow 3\mathrm{CO_2} + 3\mathrm{H_2O} \tag{447}$$

if $\xi = 0.1$ mol then 0.1 mol of $\mathrm{C_3H_6O_3}$ 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

$$0 = \sum_{\alpha=1}^{m} \sum_{i=1}^{k} \mu_i^{\alpha}\, dn_i^{\alpha} \tag{448}$$

$$= \sum_{i=1}^{k} \sum_{\alpha=1}^{m} \mu_i^{\alpha}\, dn_i^{\alpha} \tag{449}$$

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:

$$0 = \sum_{i=1}^{k} \mu_i \sum_{\alpha=1}^{m} dn_i^{\alpha} \tag{450}$$

$$= \sum_{i=1}^{k} \mu_i \, dn_i \tag{451}$$

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

$$0 = d\xi \sum_{i=1}^{k} \mu_i \nu_i \tag{452}$$

or, dividing by $d\xi$,

$$\sum_{i=1}^{k} \mu_i \nu_i = 0. \tag{453}$$

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 measureable quantities. I want next to examine chemical equilibria in ideal gas mixtures, giving a concrete example of the power of the chemical potential idea.

21 Reaction equilibrium in ideal gases

We saw earlier that for a pure ideal gas at pressure p, the chemical potential $\mu = \mu^{\ominus} + RT \ln(p/p^{\ominus})$, where $\mu^{\ominus}$ is the chemical potential at pressure $p^{\ominus}$. 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

$$\mu_i(T) = \mu_i^{\ominus}(T) + RT \ln\left(\frac{p_i}{p^{\ominus}}\right) \tag{454}$$

The equilibrium condition, Eq. (453), becomes

$$\sum_{i=1}^{k} \nu_i \left[\mu_i^{\ominus}(T) + RT \ln\left(\frac{p_i}{p^{\ominus}}\right)\right] = 0 \tag{455}$$

Collecting the standard-state chemical potentials on the left, I have

$$\sum_{i=1}^{k} \nu_i \mu_i^{\ominus}(T) = -RT \sum_{i=1}^{k} \nu_i \ln\left(\frac{p_i}{p^{\ominus}}\right) \tag{456}$$

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:

$$\sum_{i=1}^{k} \nu_i \mu_i^{\ominus}(T) = \sum_{i=1}^{k} \nu_i G_{i,\mathrm{m}}^{\ominus}(T) = \Delta_{\mathrm{r}} G_T^{\ominus} \tag{457}$$

Now we have

$$\Delta_{\mathrm{r}} G_T^{\ominus} = -RT \sum_{i=1}^{k} \nu_i \ln\left(\frac{p_i}{p^{\ominus}}\right) \tag{458}$$

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

$$\Delta_{\mathrm{r}} G_T^{\ominus} = -RT \ln \prod_{i=1}^{k} \left(\frac{p_i}{p^{\ominus}}\right)^{\nu_i} \tag{459}$$

This is a very familiar equation, though you might not recognize it yet! Take, as an example, the ideal gas reaction

$$a\mathrm{A} + b\mathrm{B} \longrightarrow c\mathrm{C} + d\mathrm{D} \tag{460}$$

Now $\nu_a = -a$, $\nu_c = c$, and so on, and we have

$$\Delta_{\mathrm{r}} G_T^{\ominus} = -RT \ln\left(\frac{(p_{\mathrm{C}}/p^{\ominus})^c (p_{\mathrm{D}}/p^{\ominus})^d}{(p_{\mathrm{A}}/p^{\ominus})^a (p_{\mathrm{B}}/p^{\ominus})^b}\right). \tag{461}$$

You should recognize the standard pressure equilibrium constant,

$$K_p^{\ominus} = \left(\frac{(p_{\mathrm{C}}/p^{\ominus})^c (p_{\mathrm{D}}/p^{\ominus})^d}{(p_{\mathrm{A}}/p^{\ominus})^a (p_{\mathrm{B}}/p^{\ominus})^b}\right), \tag{462}$$

where all the species pressures are equilibrium values. In the more general notation,

$$K_p^{\ominus} = \prod_{i=1}^{k} \left(\frac{p_i}{p^{\ominus}} \right)^{\nu_i} \tag{463}$$

Our equilibrium condition is now

$$\Delta_{\mathrm{r}} G_T^{\ominus} = -RT \ln K_p^{\ominus}(T) \tag{464}$$

and we have derived the existence of a standard equilibrium constant that depends only on T.

First, an Erratum: beginning with Eq. (456), I dropped a very important minus sign that should be in front of every RT term from there to here. Eq. (464) should read

$$\Delta_{\mathrm{r}} G_T^{\ominus} = -RT \ln K_p^{\ominus}(T)$$

21.1 Temperature dependence of ideal gas equilibrium

Eq. (464) is the fundamental connection between tabulated thermodynamic data and the practical calculation of equilibrium constants for ideal gases. In real gases and solutions we cook up "adjusted" variables—fugacities and activities—to make the formulas look similar, but here in the clean, comfortable world of ideal gases we need no such complex cuisine.

Solving Eq. (464) for $\ln K_p^{\ominus}(T)$ and differentiating both sides with respect to T gives us

$$\frac{d \ln K_p^{\ominus}(T)}{dT} = \frac{\Delta_{\mathrm{r}} G^{\ominus}}{RT^2} - \frac{1}{RT}\frac{d(\Delta_{\mathrm{r}} G^{\ominus})}{dT} \tag{465}$$

Since the overall reaction Gibbs energy is

$$\Delta_{\mathrm{r}} G^{\ominus} = \sum_i \nu_i G_{\mathrm{m},i}^{\ominus} \tag{466}$$

we have

$$\frac{d(\Delta_{\mathrm{r}} G^{\ominus})}{dT} = \frac{d}{dT}\sum_i \nu_i G_{\mathrm{m},i}^{\ominus} = \sum_i \nu_i \frac{dG_{\mathrm{m},i}^{\ominus}}{dT} \tag{467}$$

Our thermodynamic relations table gives $\left(\frac{\partial G}{\partial T}\right)_p = -S$, and the $^{\ominus}$ symbol restricts us to constant p so that the total derivatives with respect to T are the same as partial derivatives; we therefore have

$$\frac{dG_{\mathrm{m},i}^{\ominus}}{dT} = -S_{\mathrm{m},i}^{\ominus} \tag{468}$$

and

$$\frac{d(\Delta_{\mathrm{r}} G^{\ominus})}{dT} = -\sum_i S_{\mathrm{m},i}^{\ominus} = \Delta_{\mathrm{r}} S^{\ominus} \tag{469}$$

Substituting that result into Eq. (465) gives

$$\frac{d\ln K_p^{\ominus}(T)}{dT} = \frac{\Delta_r G^{\ominus}}{RT^2} + \frac{\Delta_r S^{\ominus}}{RT} \tag{470}$$

$$= \frac{\Delta_r G^{\ominus} + T\Delta_r S^{\ominus}}{RT^2} \tag{471}$$

$$\frac{d\ln K_p^{\ominus}(T)}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2} \tag{472}$$

which is the ideal gas version of the *van't Hoff equation*. It is one of the most important relations in practical thermodynamics; it describes the temperature dependence of equilibrium constants.

To experimentally evaluate $\Delta_r H^{\ominus}$ of a reaction, you measure the partial pressures of the reactants and products at several different temperatures, from those calculate the equilibrium constants, and then fit them to Eq. (472). The most common sort of fit is the old make-it-a-straight-line-dammit variety; because

$$\frac{d(1/T)}{dT} = -\frac{1}{T^2}, \tag{473}$$

Eq. (472) can equally well be written

$$\frac{d\ln K_p^{\ominus}(T)}{d(1/T)} = -\frac{\Delta_r H^{\ominus}}{R}. \tag{474}$$

So if you plot $\ln K_p^{\ominus}(T)$ against $1/T$, the slope of the plot at any T gives $\Delta_r H^{\ominus}$ at that T. If, as is usually the case over modest temperature ranges, $\Delta_r H^{\ominus}$ is roughly constant with T, then the plot will give a straight line.

21.2 Examples

I want to give several explicit examples of ideal gas equilibrium calculations. I will use the reaction

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{475}$$

as my test case.

21.2.1 Evaluating thermodynamic quantities from tables

First of all, let's find $\Delta_r G^{\ominus}_{298}$ and $K^{\ominus}_{p,298}$ for the reaction. In Table 2.6 in the back of Atkins, we find the values given in Table 6, all for 298 K:

Table 6 Thermodynamic values at 298 K for nitrogen dioxide and dinitrogen tetroxide, from the Appendix of Atkins.

	$\Delta_f G^{\ominus}$ / kJ mol^{-1}	$\Delta_f H^{\ominus}$ / kJ mol^{-1}	$C^{\ominus}_{p,m}$ / J mol^{-1} K^{-1}
NO_2	51.31	33.18	37.20
N_2O_4	97.89	9.16	77.28

We can calculate $\Delta_r G^{\ominus}_{298}$ immediately:

$$\Delta_r G^{\ominus}_{298} = 2\Delta_f G^{\ominus}(NO_2) - \Delta_f G^{\ominus}(N_2O_4) \tag{476}$$

$$= 2(51.31\,\mathrm{kJ\,mol^{-1}}) - 97.89\,\mathrm{kJ\,mol^{-1}} \tag{477}$$

$$= 4.73\,\mathrm{kJ\,mol^{-1}} \tag{478}$$

Now it is a short step to the equilibrium constant:

$$K^{\ominus}_{p,298} = e^{-\frac{\Delta_r G^{\ominus}_{298}}{RT}} \tag{479}$$

$$= e^{-1.91} \tag{480}$$

$$= 0.148 \tag{481}$$

Now, what if we need the equilibrium constant at a different temperature, say 375 K? We have several options, and the best choice depends on the available data, the temperature range, the molecules at hand, and the required precision.

Constant ΔH In the crudest approximation, we might assume that the enthalpy of reaction, $\Delta_r H^\circ$, is constant over the temperature range of interest. This is not a bad approximation if the temperature range is small. With this approximation, the van't Hoff equation can be integrated directly to get the change in the equilibrium constant. The van't Hoff equation is

$$\frac{d\ln K_p^\circ}{dT} = \frac{\Delta_r H^\circ}{RT^2} \tag{482}$$

If we assume $\Delta_r H^\circ$ is independent of T, then this equation can be integrated to give

$$\begin{aligned}
d\ln K_p^\circ &= \frac{\Delta_r H^\circ}{RT^2}\,dT && (483)\\
\ln K_p^\circ(T_2) - \ln K_p^\circ(T_1) &= \int_{T_1}^{T_2} \frac{\Delta_r H^\circ}{RT^2}\,dT && (484)\\
&= \frac{\Delta_r H^\circ}{R}\int_{T_1}^{T_2}\frac{dT}{T^2} && (485)\\
&= -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) && (486)\\
\ln K_p^\circ(T_2) &= \ln K_p^\circ(T_1) - \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) && (487)
\end{aligned}$$

We already have $\ln K_p^\circ(298) = -1.91$; to find the equilibrium constant at 375 K we need $\Delta_r H^\circ$. From Table 6 we have

$$\begin{aligned}
\Delta_r H_{298}^\circ &= 2\Delta_f H^\circ(\mathrm{NO_2}) - \Delta_f H^\circ(\mathrm{N_2O_4}) && (488)\\
&= 2(33.18\,\mathrm{kJ\,mol^{-1}}) - 9.16\,\mathrm{kJ\,mol^{-1}} && (489)\\
&= 57.20\,\mathrm{kJ\,mol^{-1}}. && (490)
\end{aligned}$$

giving us

$$\begin{aligned}
\ln K_p^\circ(375\,\mathrm{K}) &= -1.91 - \frac{57.20\times 10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{375\,\mathrm{K}} - \frac{1}{298\,\mathrm{K}}\right) && (491)\\
&= -1.91 + 4.74 && (492)\\
&= 2.83 && (493)
\end{aligned}$$

so that

$$K_p^\circ(375\,\mathrm{K}) = e^{2.83} = 16.95. \tag{494}$$

Constant ΔC_p If the temperature range is wider, it may not be adequate to assume that $\Delta_r H^\circ$ is constant over the whole range. At the next level of approximation, we can assume instead that the heat capacities of the reactants and products are constant. For example, for ordinary diatomic gases, $C_{p,\mathrm{m}} = \frac{7}{2}R$ quite accurately from about 100 K to 2000 K. In our example problem, this assumption is not so good because there are low-frequency vibrations in N_2O_4 that are not all in $v = 0$ over our temperature range. Nonetheless, let's try it.

We want to calculate $\Delta_r H^\circ(T)$, so we follow the procedure outlined in Section 12.5.2. We use

$$\Delta_r H^\circ(T_2) = \int_{T_2}^{T_1} C_p^{\text{reactants}}(T)\,dT + \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} C_p^{\text{products}}(T)\,dT \quad (495)$$

$$= \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} (C_p^{\text{products}}(T) - C_p^{\text{reactants}}(T))\,dT \quad (496)$$

$$= \Delta_r H^\circ(T_1) + \Delta C_p \int_{T_1}^{T_2} dT \quad (497)$$

$$= \Delta_r H^\circ(T_1) + \Delta C_p(T_2 - T_1) \quad (498)$$

Now I need to use this expression in the van't Hoff equation to find the equilibrium constant at 375 K. Letting $T_1 \to 298$ and $T_2 \to T$, I have

$$d\ln K_p^\circ = \frac{\Delta_r H^\circ}{RT^2}\,dT \quad (499)$$

$$= \frac{\Delta_r H^\circ(298) + \Delta C_p(T - 298)}{RT^2}\,dT \quad (500)$$

$$\ln K_p^\circ(375) - \ln K_p^\circ(298) = \int_{298}^{375} \frac{\Delta_r H^\circ(298) + \Delta C_p(T - 298)}{RT^2}\,dT \quad (501)$$

$$= -\frac{\Delta_r H^\circ(298)}{R}\left(\frac{1}{375} - \frac{1}{298}\right) + \frac{\Delta C_p}{R}\int_{298}^{375} \frac{(T - 298)}{T^2}\,dT \quad (502)$$

$$= -\frac{\Delta_r H^\circ(298)}{R}\left(\frac{1}{375} - \frac{1}{298}\right) + \frac{\Delta C_p}{R}\left[\ln T + \frac{298}{T}\right]_{298}^{375} \quad (503)$$

$$= 4.74 + \frac{\Delta C_p}{R}\left[\ln\left(\frac{375}{298}\right) + 298\left(\frac{1}{375} - \frac{1}{298}\right)\right] \quad (504)$$

Table 6 gives us

$$\Delta C_p = 2(37.20) - 77.28 = -2.88\,\mathrm{J\,K^{-1}\,mol^{-1}}, \quad (505)$$

where the "per mole" in the units refers to moles of N_2O_4. We therefore have

$$\ln K_p^{\ominus}(375) = -1.91 + 4.74 + 0.071 \tag{506}$$

$$= 2.90, \tag{507}$$

so that $K_p^{\ominus}(375) = 18.2$.

Integration with accurate C_p It is not always reasonable to assume that the heat capacities are constant, especially over wide temperature ranges. In that case, we still use Eq. (496), but must find expressions for the heat capacities of products and reactants as functions of T. The NIST WebBook gives the following equation (and a handy Java program for generating plots or tables of data as a function of T) for the heat capacity of N_2O_4:

$$C_{p,\mathrm{m}}^{\ominus} = A + Bt + Ct^2 + Dt^3 + E/t^2, \tag{508}$$

where $t = T/1000\,\mathrm{K}$. Two different sets of coefficients A–E are specified, one for the temperature range 500–1000 K, and the other for the range 1000–6000 K. Neither of them covers our range of interest. In a pinch, we could try interpolating between the data in that table, beginning at 500 K, and the $C_{p,\mathrm{m}}$ given in Atkins at 298 K. Instead let's go on to calculating equilibrium properties from the better of the two estimates we have.

21.2.2 Equilibrium calculations

Let us calculate the mole fractions of NO_2 and N_2O_4 in an equilibrium mixture at 375 K and (1) fixed total pressure, and (2) fixed volume, with an initial pressure of N_2O_4 of 10 bar and no NO_2 in both cases.

I will give quantities referring to N_2O_4 a subscript 2 and those referring to NO_2 a subscript 1. In the fixed-total-pressure version (this is what happens if you enclose the gases in a balloon), this two-gas system can be solved very easily. We have $p_1 + p_2 = p_{\mathrm{tot}}$, so

$$K_p^{\ominus} = \frac{(p_1/p^{\ominus})^2}{p_2/p^{\ominus}} \tag{509}$$

$$= \frac{(p_1/p^{\ominus})^2}{(p_{\mathrm{tot}} - p_1/p^{\ominus}} \tag{510}$$

$$\tag{511}$$

That gives a quadratic equation for p_1; solving it numerically (quicker, for me, than using the quadratic formula) gives $p_1 = 7.17$ bar. Since the total pressure is 10 bar, I have $x_1 = 0.717$ and $x_2 = 0.293$.

In the constant volume case, let me show a more systematic approach. Let z be the extent of reaction at equilibrium. Then we can set up an "ICE table", as in general chemistry:

	n_2	n_1
initial	ap_i	0
change	$-z$	$2z$
equilibrium	$ap_i - z$	$2z$
p_e	$p_i - z/a$	$2z/a$

where $a = V/RT$ and p_i is the initial pressure of N_2O_4. Now we can write an expression for $K_p^{\ominus}$ in terms of z:

$$K_p^{\ominus} = \frac{(2z/ap^{\ominus})^2}{(p_i - z/a)/p^{\ominus}} \tag{512}$$

$$K_p^{\ominus} p^{\ominus} = \frac{(2z/a)^2}{p_i - z/a} \tag{513}$$

$$\tag{514}$$

At this point it is useful to define a new variable $y = z/a$. Then we have

$$K_p^{\ominus} p^{\ominus} = \frac{4y^2}{p_i - y} \tag{515}$$

We have values for everything in that equation except y; it's a quadratic equation in y. You can solve it with the quadratic formula, or numerically; I would tend to do the latter. Setting up my calculator to evaluate

$$f(y) = \frac{4y^2}{10 - y} - 18.2, \tag{516}$$

I find that $y = 5$ gives a positive result and $y = 4$ gives a negative result, so the root must lie between those two numbers. Searching in that range, after a minute or so I have $y = 4.84368$ to five places. (In the next section I'll show you how to get all those decimal places very fast.)

With that result I can go back to find the mole fractions. We now know that $y = z/a = 4.84368$. The equilibrium mole fraction of N_2O_4 is then

$$x_2 = \frac{ap_i - z}{ap_i - z + 2z} = \frac{ap_i - ay}{ap_i + ay} = \frac{p_i - y}{p_i + y} = 0.347, \tag{517}$$

and since this is a 2-component system we have

$$x_1 = 1 - x_2 = 0.653. \tag{518}$$

(Of course we could also calculate x_1 explicitly, like we did for x_2.)

This ICE table approach, writing $a = V/RT$ to convert numbers of moles to pressure, is the general method for constant-volume problems. In constant-pressure problems, you go from the equilibrium numbers of moles in the ICE table to equilibrium pressures by writing expressions for the mole fractions in terms of z, then multiplying each mole fraction by p_{tot}. In both cases you end up with a single-variable equation to solve for z (or $y = z/a$).

Finding roots of functions of a single variable When you have a quadratic equation, as in the problem we just did, you can find the roots using the quadratic formula you learned in high school. There will be two roots; only one of them will lie in the range of z that is acceptable from a limiting-reagent standpoint. That is, only one of the two will give positive numbers of moles for all components at equilibrium.

For many problems, you end up with equations of higher degree; in the homework, for example, you get a fourth-degree equation. There is a "quartic formula", like the quadratic formula, but it's messy, and there's no formula for equations of fifth degree or higher. I find it fast and comfortable to find roots of such equations numerically.

It helps if you can get a good estimate of z ahead of time. If the equilibrium constant is small, for example, and you started with no products in the mixture, then you expect the overall extent of reaction to be small and you can use the approximation so popular in weak acid-base chemistry, neglecting z whenever it is added to a larger number.

Lacking such an estimate, the first task is to *bracket* the root: find two values of z within the acceptable range that produce function values of opposite sign. In the example above, I used the function

$$f(y) = \frac{4y^2}{10 - y} - 18.2,$$

and found that $y = 4$ gave a negative $f(y)$ and $y = 5$ a positive one; I therefore knew that the root lay somewhere between those two numbers. Call them the lower and upper limits.

At this point, the most natural approach to choose is *bisection*. Try the value of y halfway between the two limits (4.5 in this case). The function will come out either positive or negative. Replace whichever limit gave a function value of that sign with the trial value. In my case, $f(y)$ is negative at 4.5, so my new limits are $4.5 < y < 5$. You can keep going in that way, halving the width of the interval with each iteration.

Bisection gets you successive significant figures linearly with effort: it takes about three iterations to get each new significant figure. It is also foolproof; once you have a bracket, with function values of opposite signs on the two sides, there is no way bisection can fail.

If you want high precision, it is worth going to *Newton's method.* Its disadvantage is that if you do not have a good initial guess, it can fail altogether; its advantage is that if you do have a good initial guess, it converges extremely fast, the number of significant figures doubling at each iteration. Within two or three iterations you are at the precision limit of your calculator.

Newton's method works like this. If you have an equation $f(x) = 0$, and you have a guess at the root x_0, then you get a new-and-improved guess by calculating

$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}, \tag{519}$$

where f' is the derivative of $f(x)$. In my example, if I have used bisection to get to $4.8 < y < 4.9$, I might use 4.85 as my initial guess. I rewrite $f(y)$ as

$$4y^2 + 18.2y - 182, \tag{520}$$

so I calculate my next value as

$$y_1 = y_0 - \frac{4y^2 + 18.2y - 182}{8y + 18.2}. \tag{521}$$

Putting in 4.85 I get back 4.843684211; putting that value in as y_0 gives 4.843681409 which is all the precision my calculator has. (Of course, it's also far more precision than my three-sig-fig equilibrium constant justifies!)

Trapezoidal rule integrations It is also valuable to be able to do numerical integrals in a simple way. If you have a table of values of y as a function of x, and no handy way to get new values of y at x of your own choosing, then it's hard to do much better than the *trapezoidal rule*:

$$\int_{x_0}^{x_n} f(x)\,dx \approx \sum_{i=1}^{n} \frac{1}{2}(f(x_i) + f(x_{i-1}))(x_i - x_{i-1}) \tag{522}$$

Figure 24 shows how this works. I set it up in a spreadsheet on the solution set to this week's homework to evaluate the change in $\Delta_{\mathrm{r}}H^{\ominus}$ with temperature, so you can see how it gets implemented in that case.

Figure 24: The trapezoidal rule for numerical integration. The x-axis gets broken into segments (probably at the tabulated x_i), and within each segment the area is treated as a trapezoid. The area of the trapezoid is the width times the average of the heights at the two sides.

22 Equilibrium in real gases and solutions

22.1 Definition of activity

For ideal gases we found that

$$\mu_i = \mu_i^{\ominus}(T) + RT\ln\left(\frac{p_i}{p^{\ominus}}\right) \tag{523}$$

and from that

$$\Delta G_T^{\ominus} = \sum_i \nu_i \mu_i^{\ominus}(T) = -RT\ln K_p^{\ominus} \tag{524}$$

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

$$\mu_i = \mu_i^{\ominus}(T) + RT\ln a_i, \tag{525}$$

where $\mu_i^{\ominus}(T)$ 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 $\mu_i^{\ominus}(T)$ clearly does, the activity a_i will as well.

With this definition of activity we will, by the same procedure as before, find that there is an equilibrium constant with the form

$$K^{\ominus} = \prod_i a_i^{\nu_i}. \tag{526}$$

22.2 Real gas activities: the fugacity

Eq. (525) 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

$$\mu_i = \mu_i^{\ominus}(T) + RT\ln\left(\frac{f_i}{p^{\ominus}}\right), \tag{527}$$

that is, $a_i = f_i/p^{\ominus}$. 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

$$\ln \phi(p) = \int_0^p \left(\frac{Z(p') - 1)}{p'} \right) dp' \tag{528}$$

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 ed. (McGraw-Hill, 1987).

With fugacity coefficients in hand, we have

$$K^\ominus = \prod_i \left(\frac{f_i}{p^\ominus} \right)^{\nu_i} = \prod_i \left(\frac{\phi_i p_i}{p^\ominus} \right)^{\nu_i}, \tag{529}$$

which can be factored to give

$$\frac{K^\ominus}{\prod_i (\phi_i)^{\nu_i}} = \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i}. \tag{530}$$

A sensible way to evaluate equilibrium pressures in reacting real gas mixtures is as follows. You calculate $K^\ominus$ in the usual way from tabulated values of $\Delta_f G_T^\ominus$, 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" $K^\ominus$ 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 terribly far from ideal.

22.3 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.

22.3.1 Raoult's Law

I will follow the convention of Atkins (and some other authors) and denote 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)

$$\mu_A^* = \mu_A^\ominus + RT\ln\left(\frac{p_A^*}{p^\ominus}\right) \tag{531}$$

where $\mu_A^\ominus$ 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

$$\mu_A = \mu_A^\ominus + RT\ln\left(\frac{p_A}{p^\ominus}\right) \tag{532}$$

Eliminating $\mu_A^\ominus$ between those two equations gives

$$\mu_A = \mu_A^* + RT\ln\left(\frac{p_A}{p_A^*}\right) \tag{533}$$

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,

$$p_{\mathrm{A}} = x_{\mathrm{A}} p_{\mathrm{A}}^{*}. \tag{534}$$

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. (534).

Substituting Eq. (534) into Eq. (533) gives

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{*} + RT \ln x_{\mathrm{A}}. \tag{535}$$

We will use this equation shortly to define activity coefficients for nonideal solutions.

22.3.2 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

$$p_{\mathrm{B}} = x_{\mathrm{B}} K_{\mathrm{B}}, \tag{536}$$

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 7.15 in Atkins shows how Raoult's and Henry's Laws apply to a real solution; 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 25 shows some other cases.

Figure 25: 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).

22.4 Activity conventions for solvents and solutes

22.4.1 Solvent activities

Eq. (533) 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

$$\mu_A = \mu_A^* + RT\ln x_A. \tag{537}$$

But even if the solution is not ideal, we can write instead

$$\mu_A = \mu_A^* + RT\ln a_A, \tag{538}$$

with

$$a_A = \frac{p_A}{p_A^*}, \tag{539}$$

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

$$a_A = \gamma_A x_A, \tag{540}$$

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

$$\gamma = \frac{x_{\text{vapor}} p_{\text{tot}}}{x_{\text{liquid}} p^*} \tag{541}$$

$$= \frac{(.1434)(262)}{(.2003)(344.5)} \tag{542}$$

$$= 0.544 \tag{543}$$

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.

22.4.2 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

$$a_B = \frac{p_B}{K_B} \tag{544}$$

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.

22.5 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

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{\ominus} + RT \ln \frac{b}{b^{\ominus}}, \tag{545}$$

where b indicates the molality of the solution, $b^{\ominus}$ is the "standard molality" (one mol/kg), and $\mu_{\mathrm{B}}^{\ominus}$ is the chemical potential of B in the "molality-scale standard state", which is an imaginary state in which the concentration of B is 1 molal but it behaves as though it was at very high dilution.

23 Electrochemistry

In an electrochemical cell, it is possible to separate the two half-reactions that take place during a redox reaction. The electrons that leave the oxidized species travel through wires before arriving at the position of the other species and reducing it.

23.1 Standard thermodynamic functions for ions

There are only a few new thermodynamic ideas associated with electrochemistry. The first is that enthalpies and entropies of formation of aqueous ions, unlike those of neutral compounds, cannot be determined individually; any ionic solution contains both positive and negative ions. Therefore, ion thermodynamic properties are conventionally determined by defining the standard enthalpy, entropy, and Gibbs energy of formation of $\mathrm{H}^+(aq)$ to be zero, and determining all the thermodynamic properties of other ions by comparison. For example, Atkins shows how to determine the Gibbs energy of formation of chloride ion. We measure (experimentally, by calorimetry) the enthalpy and entropy changes in the reaction

$$\frac{1}{2}\mathrm{H}_2(g) + \frac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{H}^+(aq) + \mathrm{Cl}^-(aq). \tag{546}$$

The experimental $\Delta_r H^\circ_{298}$ for that reaction is -167.16 kJ mol^{-1}; since the enthalpy of formation of $\mathrm{H}^+(aq)$ is defined to be zero, and since both reactants are elements in their standard states, that value is the enthalpy of formation of aqueous chloride ion. Now a calorimetric measurement on another reaction involving $\mathrm{H}^+(aq)$, $\mathrm{Cl}^-(aq)$, and elements, that consumes or produces another ion, will yield the enthalpy of formation of that ion, and so on. All the aqueous ion thermodynamic properties in Table 2.6 of Atkins were determined that way.

Standard entropies of ions are determined using the same convention. For this reason, entropy entries for ions in thermodynamic tables sometimes show negative values (which never appear for neutral compounds, since their reference state is the pure compound at 0 K, and heat must always be added to bring them to the standard temperature). A negative standard entropy for an aqueous ion implies that a solution of that ion has lower entropy than a solution of $\mathrm{H}^+(aq)$ at the same temperature and pressure.

23.2 Electrochemical cells

In an electrochemical cell, we have two electrodes (chunks of metal, often different metals) immersed in electrolyte solutions. Both electrodes can be in one solution, or they can be in different solutions connected by a *salt bridge*, which allows ions (positive or negative) to flow from one "compartment" to another without allowing the solutions to mix. At one of the electrodes (the anode), electrons flow from the solution (or, sometimes, a gas or insoluble salt in contact with the electrode) into the electrode. At the other electrode (the cathode), electrons flow from the electrode into the material surrounding it.

If the two electrodes are in separate compartments, some ions must flow from one compartment to another to keep charges from building up on the two sides. That is the purpose of the salt bridge; often, inert salts (for example, potassium chloride) are added to the solutions and the salt bridge for this purpose.

In the standard notation for electrochemical cells, the electrode materials are written at the ends, with the materials separating them listed in order.. Each phase boundary is specified by a vertical line; a phase boundary with no *junction potential* (change in electrical potential from one side of the boundary to the other, usually produced by a salt bridge) is given a double vertical line. The "Daniell cell", an early battery, is written

$$\mathrm{Zn}(s)|\mathrm{ZnSO_4}(aq)||\mathrm{CuSO_4}(aq)|\mathrm{Cu}(s) \tag{547}$$

and shown in Figure 26. The reaction at the cathode (a reduction) is

$$\mathrm{Cu^{2+}}(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{Cu}(s) \tag{548}$$

while that at the anode is

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(aq) \tag{549}$$

Electrochemical half-reactions are nearly always written as reductions (with the electrons as reactants, not products), so in a table you would find the Zn reaction written the other way around. The overall reaction is

$$\mathrm{Cu^{2+}}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{Zn^{2+}}(aq) \tag{550}$$

That reaction is spontaneous; if you stick a piece of zinc into a solution of copper sulfate, metallic copper will appear on the zinc rod. If you take two beakers, fill one with zinc sulfate solution and one with copper sulfate solution, connect them with a salt bridge, stick a zinc rod in the first and a copper rod in the second, and connect a high-quality voltmeter across the two electrodes, you will read a "cell potential" of over a volt (with the copper rod being positive with respect to the zinc.) I next want to show how to predict those things from tabulated information.

Figure 26: The Daniell cell with salt bridge; cf. Atkins figures 10.9 and 10.10.

23.3 Cell potential and the Nernst equation

The link between electrochemical measurements and the Gibbs energy is the formula for the amount of work required to move a charge through a potential difference: $w = q\Delta V$. That idea, plus the role of the Gibbs energy as the maximum non-PV work obtainable from a system, leads quickly to the crucial formula

$$-\nu FE = \Delta_\mathrm{r} G, \tag{551}$$

where ν is the number of electrons transferred in the reaction from anode to cathode, F is the Faraday constant (the charge on a mole of electrons: 96485.3 C mol^{-1}), and E is the *zero-current cell potential* (also called "electromotive force" or just emf), the voltage you measure across the cell electrodes if no current is flowing. (It's unfortunate that electrochemists use E rather than V for the cell potential, in my opinion.)

Writing the change in Gibbs energy for a reaction in terms of the standard-state Gibbs energy change, we have

$$\Delta_\mathrm{r} G = \Delta_\mathrm{r} G^\ominus + RT \ln Q, \tag{552}$$

where Q is the usual ratio of product and reactant activities raised to their stoichiometric powers. Dividing both sides by $-\nu F$, and defining

$$E^\ominus = -\frac{\Delta_\mathrm{r} G^\ominus}{\nu F}, \tag{553}$$

we arrive at the *Nernst equation*:

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q. \tag{554}$$

The Nernst equation tells us how the observed potential of the cell will change with cell composition. If the reaction reaches equilibrium, $Q = K$, the cell is no longer capable of doing work so $E = 0$, and we have

$$E^\ominus = \frac{RT}{\nu F} \ln K \tag{555}$$

Now, how do we find $E^\ominus$? Easy: we look up reduction potentials for the two half-reactions occuring in the cell, invert the sign for the oxidation reaction, and add the two together. Notice that if you have a system where one half-reaction must occur twice to allow the other to occur once, it is not necessary to multiply the first standard potential by 2; that is taken care of by the ν term in Eq. (554). Standard reduction potentials are written assuming a standard state with all ions at 1 molal concentration but ideally-dilute behavior, so the equilibrium constants come out with activities on the molality scale.

Notice that Eq. (553) indicates that if an overall reaction has $E^\ominus > 0$, then $\Delta_\mathrm{r} G^\ominus < 0$ and the reaction is spontaneous as written (that is, will proceed to the right).

Example: K for simple redox reaction Let us evaluate the equilibrium constant for the reaction

$$\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) \rightleftharpoons \mathrm{Fe}^{2+}(aq) + \mathrm{Mn}^{3+}(aq). \tag{556}$$

For this case the two half-reactions (written as reductions) are simple:

$$\mathrm{Fe}^{3+}(aq) + \mathrm{e}^- \longrightarrow \mathrm{Fe}^{2+}(aq) \qquad \mathrm{E}^\ominus = +0.77\,\mathrm{V} \tag{557}$$

$$\mathrm{Mn}^{3+}(aq) + \mathrm{e}^- \longrightarrow \mathrm{Mn}^{2+}(aq) \qquad \mathrm{E}^\ominus = +1.51\,\mathrm{V} \tag{558}$$

The standard cell potential is therefore $0.77 - 1.51 = -0.74$ V. The equilibrium constant is

$$\ln K = \frac{\nu F E^{\ominus}}{RT} \tag{559}$$

The value of RT/F at 298 K is 0.025693 V, and $\nu = 1$, so

$$\ln K = \frac{-0.74\,\mathrm{V}}{0.025693\,\mathrm{V}} \tag{560}$$

$$= -28.8 \tag{561}$$

$$K = 3.1 \times 10^{-13} \tag{562}$$

This reaction equilibrium lies to the left as written; the reaction mixture will be mostly reactants at equilibrium.

24 Temperature Dependence of Rates

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

$$k = Ae^{-E_a/RT} \tag{563}$$

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. The parameters A and E_a should be regarded as empirical quantities with the *definitions*

$$E_a(T) = -R\frac{d(\ln k)}{d(1/T)} \tag{564}$$

$$= RT^2\frac{d(\ln k)}{dT} \tag{565}$$

$$A(T) = k(T)/\exp(-E_a(T)/RT) \tag{566}$$

The necessary function $k(T)$ can be obtained either from experiment or from some theory. Figure 27 shows the behavior predicted by the Arrhenius equation for the two common plots, k vs. T and $\ln(k)$ vs. $1/T$.

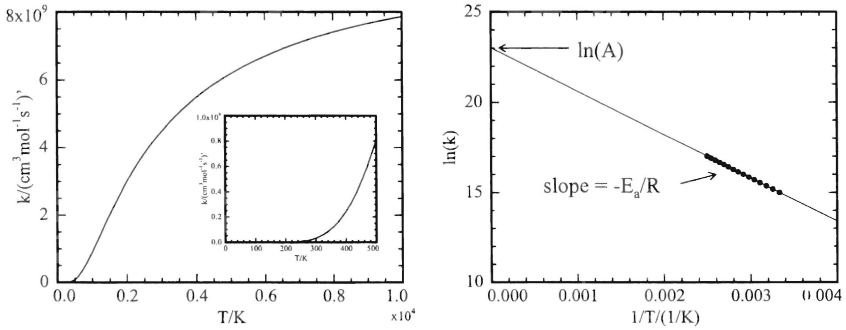

Figure 27: Two plots of rate coefficients for a reaction with $A = 10^{10}$ cm^{3}mol^{-1}s^{-1} and $E_a = 20$ kJ/mol.

Most chemists think of the activation energy E_a as a measure of the "barrier height" of the reaction. That interpretation is basically correct, though it can be misleading when the reactions studied are composite rather than elementary. A sharper interpretation, for elementary reactions, is given by *Tolman's theorem*: the activation energy is the difference between the average energy of molecules in the process of reacting and the average energy of all the molecules. There is no reason to expect, from this interpretation, that the activation energy should be independent of temperature, but temperature dependence of E_a is difficult to detect with imprecise data over limited temperature ranges. Figure 28 gives a schematic of this interpretation.

Figure 28: Tolman's theorem.

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 27.

When data of high quality are taken over a sufficiently wide temperature range, usually the Arrhenius equation does not describe them accurately; plots of $\ln k$ vs. $1/T$ are curved. In that case we speak of temperature-dependent A and E_a, as illustrated in Figure 29.

Such behavior is possible for several reasons. Most commonly, the reaction being studied is not an elementary one, and while one of the elementary steps might be the rate-limiting one at low temperature, a different

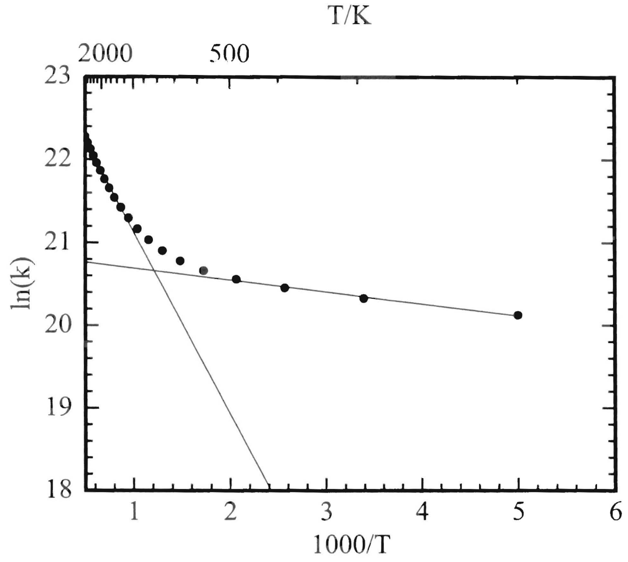

Figure 29: "Arrhenius plot" for a reaction that does not follow simple Arrhenius behavior.

one might be rate-limiting at high temperature; in that case, the slope will change from one value to another in the intermediate temperature range. (This sort of case is what I used to make the plot.) But Arrhenius plots are often curved even for elementary reactions; the way the available thermal energy is distributed among the molecules will change as T changes, and that will produce changes in the average energies described by Tolman's theorem.

Data that show curvature on Arrhenius plots are most often fitted by the equation

$$k(T) = AT^m e^{-E_b/RT}, \tag{567}$$

where the three parameters A, m, and E_b may be varied to fit the data. The values of A, m, and E_b should be regarded simply as empirical fitting constants that can be used to summarize a large quantity of kinetic data with just a few numbers. It can be misleading to try to extract chemical information from empirically fitted values. On the other hand, some theories of reaction rates make physical *predictions* of the values of A, m, and E_b.

24.1 Thermodynamic functions of activation

There is a large and relatively successful body of theory called "transition state theory" or "activated complex theory" whose initial goal was the absolute prediction of rate coefficients. That goal has been met in very limited cases, but the theory has found wide use because it provides some insight into the underlying chemistry of kinetic processes. The fundamental assumption of transition state theory is there there are molecular complexes of special types, called "transition states", that are in the process of becoming products, and these transition states are in equilibrium with reactants at all times.

This assumption makes it reasonable to talk about a sort of equilibrium constant for the conversion from ordinary reactants to transition states. If the rate of appearance of products is proportional to the concentration of transition states, then (with some work that I have left out) we get, in the most common notation,

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}, \tag{568}$$

where $\Delta S^\ddagger$ is the *entropy of activation* and $\Delta H^\ddagger$ is the *enthalpy of activation*. The enthalpy of activation is traditionally determined by an "Eyring plot", a plot of k/T against $1/T$; the slope of such a plot is $-\Delta H^\ddagger/R$. The numerical value of $\Delta H^\ddagger$ is not usually very different (perhaps by a few times RT) from that of E_a; the detailed relationship between the two depends of the type of reaction. (Should you need to know, I recommend *Chemical Kinetics*, by K. J. Laidler.) Keep in mind that these "thermodynamic functions of activation" are not true equilibrium thermodynamic properties, and cannot generally be measured with the precision of equilibrium properties such as heats of formation.

24.2 Example

The following few pages are copied from a large 1992 compilation of data on hundreds of reactions in the gas phase, intended for people setting up computer models of hydrocarbon combustion. The $OH + CH_4$ reaction has been studied for many years, and the data available for it are more numerous and of better quality than those for many other reactions; nonetheless, you can see that there is still a fair amount of scatter.

25 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 occuring.

With those two postulates you can get remarkably far. The quantity of central importance in statistical mechanics is the *partition function*:

$$Z = \sum_j e^{-E_j/k_B T}, \tag{569}$$

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:

$$U = k_B T^2 \left(\frac{\partial(\ln Z)}{\partial T}\right)_{V,N_i} \tag{570}$$

$$S = k_B T \left(\frac{\partial(\ln Z)}{\partial T}\right)_{V,N_i} + k_B \ln Z \tag{571}$$

$$A = -k_B T \ln Z \tag{572}$$

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.

25.1 Molecular partition functions

If we have a collection of identical, noninteracting molecules, then the overall partition function becomes

$$Z = \frac{z^N}{N!}, \tag{573}$$

where N is the number of molecules and z is the *molecular partition function*:

$$z = \sum_r e^{-\frac{\varepsilon_r}{k_B T}}, \tag{574}$$

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, as follows:

$$z = \sum_j g_j e^{-\frac{\varepsilon_j}{k_B T}} \tag{575}$$

where g_j is the degeneracy of level j with energy ε_j.

25.2 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

$$P_i = \frac{g_i e^{-\frac{\varepsilon_i}{k_B T}}}{z} \tag{576}$$

For example, the fraction of molecules in a sample of CO at 300 K in the rotational level J is

$$P_J = \frac{(2J+1)e^{-\frac{BJ(J+1)}{k_B T}}}{\sum_{J=0}^{\infty}(2J+1)e^{-\frac{BJ(J+1)}{k_B T}}} \tag{577}$$

With $B = 1.9225\,\mathrm{cm}^{-1}$, at 300 K we get $z = 106.9$ 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.