1 Elementary Reactions and Mechanisms

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

$$\mathrm{O} + \mathrm{CH_4} \longrightarrow \mathrm{OH} + \mathrm{CH_3}, \tag{1}$$

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

$$-\frac{d[\mathrm{O}]}{dt} = -\frac{d[\mathrm{CH_4}]}{dt} = \frac{d[\mathrm{OH}]}{dt} = \frac{d[\mathrm{CH_3}]}{dt} = k[\mathrm{O}][\mathrm{CH_4}], \tag{2}$$

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

$$2\mathrm{ICl} + \mathrm{H_2} \longrightarrow \mathrm{I_2} + 2\mathrm{HCl} \tag{3}$$

might have the observed rate law

$$\frac{1}{2}\frac{d[\mathrm{HCl}]}{dt} = k[\mathrm{ICl}][\mathrm{H_2}]. \tag{4}$$

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

$$\mathrm{ICl} + \mathrm{H_2} \xrightarrow{k_1} \mathrm{HI} + \mathrm{HCl} \qquad \text{(slow)} \tag{5}$$

$$\mathrm{HI} + \mathrm{ICl} \xrightarrow{k_2} \mathrm{HCl} + \mathrm{I_2} \qquad \text{(fast)} \tag{6}$$

We will shortly see how to analyze the behavior of this mechanism quantitatively. Note that adding together Eq. (5) and Eq. (6) 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.

1.1 Simple example: reversible unimolecular transformation

The mechanism

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{7}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{A}, \tag{8}$$

which can also be written

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}, \tag{9}$$

gives the set of "elementary rate laws"

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_2[\mathrm{B}] \tag{10}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{11}$$

This is a system of two coupled ODEs. Once the initial conditions are specified, its solution describes the complete time dependence. Figure 1 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.

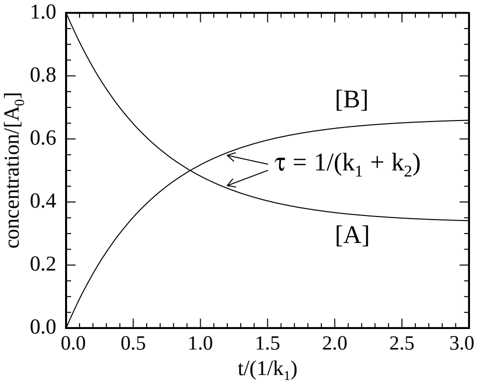

Figure 1: Behavior of a reversible first order reaction for the case $B_0 = 0$ and $k_1 = 2k_2$.

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

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_2(B_0 + A_0 - [\mathrm{A}]). \tag{12}$$

Eq. (12) is now a separable differential equation in [A] only. Its solution, with $[\mathrm{A}](t = 0) = A_0$, is

$$[\mathrm{A}](t) = \frac{1}{k_1 + k_2} \times \left\{ (k_1 A_0 - k_2 B_0) e^{-(k_1+k_2)t} + k_2(A_0 + B_0) \right\}. \tag{13}$$

The rate law in this case looks like

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_2)[\mathrm{A}] - k_2(\mathrm{B}_0 + \mathrm{A}_0) \tag{14}$$

$$= k'[\mathrm{A}] + C, \tag{15}$$

and the reaction order is not defined.

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

$$k_1[\mathrm{A}]_{\mathrm{eq}} = k_2[\mathrm{B}]_{\mathrm{eq}} \tag{16}$$

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_2} \tag{17}$$

$$= K_{\mathrm{eq}} \tag{18}$$

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

2 Exact and approximate analytic solutions to sets of rate equations.

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

2.1 Consecutive first-order reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{19}$$

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

$$\begin{aligned} \mathrm{Br}^*_{\frac{1}{2}} + \mathrm{CO}_2 &\longrightarrow \mathrm{CO}_2^*(001) + \mathrm{Br}_{\frac{3}{2}} && (20)\\ \mathrm{CO}_2^* + \mathrm{CO}_2 &\longrightarrow 2\mathrm{CO}_2, && (21) \end{aligned}$$

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^*.

A decays away with $\tau = 1/k_1$. B grows, then decays:

$$[\mathrm{B}] = \frac{k_1 \mathrm{A}_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{22}$$

where the set of rate equations was one of the problems on the math refresher assignment. The maximum concentration of B depends on the relative sizes of k_1 and k_2. Let's look at the two extreme cases, illustrated in the upper and lower panels of Figure 2.

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

In this case, then at short times ($t \gtrsim 0$), the second exponential term in Eq. (22) 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 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: $[\mathrm{C}] = A_0 - [\mathrm{A}] - [\mathrm{B}]$. Substituting the long-time behavior of B into that expression gives $C = A_0(1 - e^{-k_2 t)}$, and C grows with time constant $1/k_2$ from B.

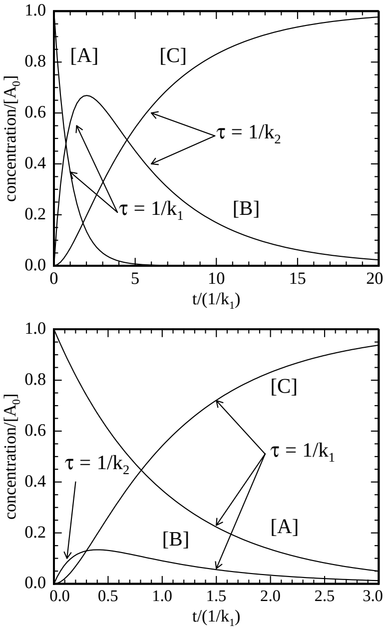

Figure 2: Temporal behavior of consecutive, irreversible first-order reactions. The upper panel shows the case $k_1 = 5k_2$; the lower panel shows the case $k_2 = 5k_1$.

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

Now, at short times, $e^{-k_1 t} \approx 1$, so $[\mathrm{B}] \approx \frac{k_1}{k_2} A_0(1 - e^{-k_2 t})$. At long times, $e^{-k_2 t} \approx 0$, and we have $[\mathrm{B}] \approx \frac{k_1}{k_2} A_0 e^{-k_1 t}$. Note that the time constants on the rising and falling part of the $[\mathrm{B}](t)$ curve have inverted: the curvature on the rising part of the curve is determined by k_2, while the curvature on the falling part is given by k_1. The faster rate coefficient always sets the exponential behavior of the rise, no matter whether it is the first or second coefficient in the mechanism.

Once again we find the behavior of C by mass balance. The exact equation, applicable no matter the values of the rate coefficients, is

$$\begin{aligned} [\mathrm{C}] &= A_0 - [\mathrm{A}] - [\mathrm{B}] && (23) \\ &= A_0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right). && (24) \end{aligned}$$

The concentration of C does not have a simple short-time behavior, but at long times $[\mathrm{C}] \approx A_0(1 - e^{-k_1 t})$. When the second rate coefficient in the consecutive mechanism is much larger than the first, then as soon as a B molecule is formed it converts right away to C, and the rising behavior of C looks as though B did not exist and C was being formed directly from A. This result anticipates the steady-state approximation.

2.2 Competetive (parallel) first order reactions

In this case, the mechanism is

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \qquad (25)$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{C} \qquad (26)$$

The rate equations are

$$\frac{d[\mathrm{A}]}{dt} = -(k_1 + k_2)[\mathrm{A}] \tag{27}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] \tag{28}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{A}] \tag{29}$$

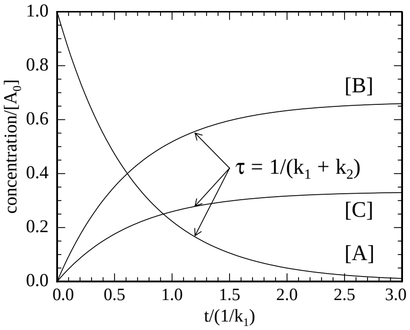

Figure 3: Temporal behavior of competing, irreversible first-order reactions. In this figure $k_1 = 2k_2$.

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:

$$[\mathrm{B}] = \frac{k_1 A_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t}) \tag{30}$$

$$[\mathrm{C}] = \frac{k_2 A_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t}) \tag{31}$$

Note that the temporal behavior of both B and C are the same; their risetimes 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.

2.2.1 Kinetic vs. thermodynamic control

If the reactions are reversible,

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{32}$$

$$\mathrm{A} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}, \tag{33}$$

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

$$\frac{[\mathrm{B}]_\mathrm{eq}}{[\mathrm{C}]_\mathrm{eq}} = \frac{[\mathrm{B}]_\mathrm{eq}}{[\mathrm{A}]_\mathrm{eq}} \cdot \frac{[\mathrm{A}]_\mathrm{eq}}{[\mathrm{C}]_\mathrm{eq}} = \frac{k_1}{k_{-1}} \frac{k_{-2}}{k_2} = K_\mathrm{BC}. \tag{34}$$

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

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

then Table 1 shows the resulting concentrations. This is a not-too-extreme case of kinetic control.

Table 1 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

2.3 Relative Rate Experiments

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

$$\mathrm{A_1 + B} \xrightarrow{k_1} \mathrm{P_1} \tag{35}$$

$$\mathrm{A_2 + B} \xrightarrow{k_2} \mathrm{P_2} \tag{36}$$

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

$$\frac{d[\mathrm{P_1}]}{dt} = k_1[\mathrm{A_1}]_0[\mathrm{B}] \tag{37}$$

$$\frac{d[\mathrm{P_2}]}{dt} = k_2[\mathrm{A_2}]_0[\mathrm{B}] \tag{38}$$

$$\frac{d[\mathrm{P_1}]}{d[\mathrm{P_2}]} = \frac{k_1[\mathrm{A_1}]_0}{k_2[\mathrm{A_2}]_0} \tag{39}$$

So, after a long time

$$\frac{[\mathrm{P_1}]_\infty}{[\mathrm{P_2}]_\infty} = \frac{k_1[\mathrm{A_1}]_0}{k_2[\mathrm{A_2}]_0} \tag{40}$$

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. (40) 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

$$\frac{d[\mathrm{A_1}]}{dt} = k_1[\mathrm{A_1}][\mathrm{B}] \tag{41}$$

$$\frac{d[\mathrm{A_2}]}{dt} = k_2[\mathrm{A_2}][\mathrm{B}]. \tag{42}$$

so

$$\frac{d[\mathrm{A}_1]}{d[\mathrm{A}_2]} = \frac{k_1}{k_2}\frac{[\mathrm{A}_1]}{[\mathrm{A}_2]} \tag{43}$$

$$k_2\frac{d[\mathrm{A}_1]}{[\mathrm{A}_1]} = k_1\frac{d[\mathrm{A}_2]}{[\mathrm{A}_2]} \tag{44}$$

$$k_2 \ln[\mathrm{A}_1] = k_1 \ln[\mathrm{A}_2] + \mathrm{C} \tag{45}$$

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

$$k_2 \ln\left(\frac{[\mathrm{A}_1]}{[\mathrm{A}_1]_0}\right) = k_1 \ln\left(\frac{[\mathrm{A}_2]}{[\mathrm{A}_2]_0}\right) \tag{46}$$

$$\frac{k_1}{k_2} = \frac{\ln\left(\frac{[\mathrm{A}_1]}{[\mathrm{A}_1]_0}\right)}{\ln\left(\frac{[\mathrm{A}_2]}{[\mathrm{A}_2]_0}\right)} \tag{47}$$

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.

2.4 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:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{48}$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{\mathrm{k}_2} \mathrm{D} \tag{49}$$

Net reaction A + C → D.

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}] \tag{50}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - (k_{-1} + k_2[\mathrm{C}])[B] \tag{51}$$

$$\frac{d[\mathrm{C}]}{dt} = -k_2[\mathrm{B}][\mathrm{C}] \tag{52}$$

$$\frac{d[\mathrm{D}]}{dt} = k_2[\mathrm{B}][\mathrm{C}] \tag{53}$$

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

$$\frac{\mathrm{d[B]}}{\mathrm{dt}} \approx 0. \tag{54}$$

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.

$$\frac{d[\mathrm{B}]}{dt} \overset{\mathrm{SSA}}{\approx} 0 = k_1[\mathrm{A}] - (k_{-1} + k_2[\mathrm{C}])[\mathrm{B}] \tag{55}$$

$$[\mathrm{B}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{A}]}{k_{-1} + k_2[\mathrm{C}]} \tag{56}$$

$$\frac{d[\mathrm{D}]}{dt} \overset{\mathrm{SSA}}{\approx} \frac{k_1 k_2[\mathrm{A}][\mathrm{C}]}{k_{-1} + k_2[\mathrm{C}]} \tag{57}$$

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

$$\frac{d[\mathrm{D}]}{dt} \overset{\mathrm{SSA}}{\approx} \frac{k_1 k_2}{k_{-1}}[\mathrm{A}][\mathrm{C}] \qquad \text{apparent 2nd order} \tag{58}$$

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

$$\frac{d[\mathrm{D}]}{dt} \overset{\mathrm{SSA}}{\approx} k_1[\mathrm{A}] \qquad \text{apparent 1st order} \tag{59}$$

2.5 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

$$(k_{-1} + k_2[\mathrm{C}]) \gg k_1. \tag{60}$$

(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

$$(k_{-1} + k_2[\mathrm{C}])t \gtrsim 5. \tag{61}$$

2.5.1 Example: sequential 1st-order reactions

In this section I want to work out a quantitative indication of the time required to establish the steady state for the simplest case. Consider

$$\mathrm{A} \xrightarrow{\mathrm{k_1}} \mathrm{B} \xrightarrow{\mathrm{k_2}} \mathrm{C}. \tag{62}$$

Then

$$[\mathrm{B}] = \frac{k_1}{k_2 - k_1} A_0 (e^{-k_1 t} - e^{-k_2 t}) \tag{63}$$

$$\frac{d[\mathrm{B}]}{dt} = \frac{A_0 k_1}{k_2 - k_1} (k_2 e^{-k_2 t} - k_1 e^{-k_1 t}) \tag{64}$$

How long until $\frac{d[\mathrm{B}]}{dt} = 0$? Call that t_S, and solve for it explicitly:

$$\ln k_2 - k_2 t_S = \ln k_1 - k_1 t_S \tag{65}$$

$$t_S(k_1 - k_2) = \ln k_1 - \ln k_2 = \ln\left(\frac{k_1}{k_2}\right) \tag{66}$$

$$t_S = \frac{1}{k_1 - k_2} \ln\left(\frac{k_1}{k_2}\right) \tag{67}$$

$$= \frac{1}{k_2 - k_1} \ln\left(\frac{k_2}{k_1}\right) \tag{68}$$

Compare this with τ for the slow step, which is $1/k_1$.

Table 2 Buildup time as a function of k_2/k_1.

k_2/k_1	2	5	10	20	50	100
t_S^*	.69	.40	.26	.16	.080	.047

$$\frac{t_S}{\tau} = t_S^* = k_1 t_S \tag{69}$$

$$t_S^* = \frac{1}{\frac{k_2}{k_1} - 1} \ln\left(\frac{k_2}{k_1}\right) \tag{70}$$

The value t_S^* indicates what fraction of the overall reaction time is required for the steady state to be established. The smaller it is, the smaller will be the error associated with the initial buildup of B. Numerical results appear in Table 2. If $k_2/k_1 \geq 50$, the steady state is established within the first ten percent of the reaction time; that is probably a reasonable cutoff for use of the approximation. In the next section I consider another approximation, the rapid equilibrium approximation, and its relation to the SSA.

2.6 Other Simplifying Approximations

Once again, consider the mechanism

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{71}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{72}$$

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

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}] \tag{73}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - (k_{-1} + k_2)[\mathrm{B}] \tag{74}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \tag{75}$$

I want to consider two main cases, illustrated in Figure 4 and summarized in Table 3.

Table 3 Relations among simplifying approximations.

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

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

The rate equations for A and B now look like the simple system $\mathrm{A} \rightleftharpoons \mathrm{B}$, whose solution was worked out in Section 1.1. After a time $\approx 1/(k_1 + k_{-1})$, the $\mathrm{A} \rightleftharpoons \mathrm{B}$ reaction will reach approximate equilibrium so that $[\mathrm{B}] \approx \frac{k_1}{k_{-1}}[\mathrm{A}]$. A and B will act like a single species that is slowly decaying toward C, and

$$\frac{d[\mathrm{C}]}{dt} \overset{\text{REA}}{\approx} \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{76}$$

This is the "rapid equilibrium approximation."

2.6.2 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

$$\frac{d[\mathrm{B}]}{dt} = -k_1[\mathrm{A}] - (k_{-1} + k_2)[\mathrm{B}] \overset{\mathrm{SSA}}{\approx} 0 \tag{77}$$

so

$$[\mathrm{B}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{A}]}{(k_{-1} + k_2)} \tag{78}$$

$$\frac{d[\mathrm{C}]}{dt} \overset{\mathrm{SSA}}{\approx} \left(\frac{k_1 k_2}{k_{-1} + k_2}\right)[\mathrm{A}] \tag{79}$$

2.6.3 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.

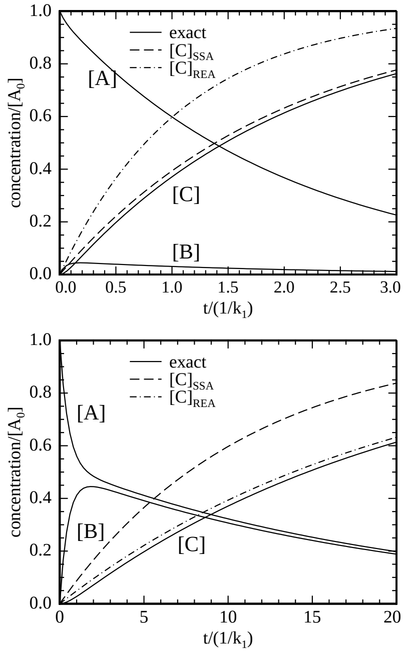

Figure 4: The steady-state and equilibrium approximations for the $A \rightleftharpoons B \longrightarrow C$ mechanism, for two different sets of rate coefficients. In the upper panel $k_{-1} = k_2 = 10k_1$; in the lower panel $k_1 = k_{-1} = 10k_2$.

2.7 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 again becomes simply k_1. 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.

2.8 Examples

2.8.1 Ligand substitution

The nucleophilic substitution reaction

$$\mathrm{Ni(CO)_4 + PPh_3 \longrightarrow Ni(CO)_3PPh_3 + CO} \tag{80}$$

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

$$\mathrm{Ni(CO)_4} \underset{\mathrm{k_{-1}}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{Ni(CO)_3 + CO} \tag{81}$$

$$\mathrm{Ni(CO)_3 + PPh_3} \xrightarrow{\mathrm{k_2}} \mathrm{Ni(CO)_3PPh_3} \tag{82}$$

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

$$\frac{d}{dt}[\mathrm{Ni(CO)_3}] = k_1[\mathrm{Ni(CO)_4}] - (k_{-1}[\mathrm{CO}] + k_2[\mathrm{PPh_3}])[\mathrm{Ni(CO)_3}] \tag{83}$$

$$[\mathrm{Ni(CO)_3}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{Ni(CO)_4}]}{k_{-1}[\mathrm{CO}] + k_2[\mathrm{PPh_3}]} \tag{84}$$

$$\frac{d}{dt}[\mathrm{Ni(CO)_3PPh_3}] = k_2[\mathrm{Ni(CO)_3}][\mathrm{PPh_3}] \tag{85}$$

$$\overset{\mathrm{SSA}}{\approx} k_2[\mathrm{PPh_3}]\frac{k_1[\mathrm{Ni(CO)_4}]}{k_{-1}[\mathrm{CO}] + k_2[\mathrm{PPh_3}]} \tag{86}$$

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

$$\frac{d}{dt}[\mathrm{Ni(CO)_3PPh_3}] \approx k_1[\mathrm{Ni(CO)_4}], \tag{87}$$

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

2.8.2 Dinitrogen pentoxide decomposition

The reaction

$$\mathrm{2N_2O_5 \rightarrow 4NO_2 + O_2} \tag{88}$$

follows an observed first-order rate law. The reaction between N_2O_5 and NO also looks first order but is much faster. NO_3, a blue gas, also appears as an intermediate. A page from Johnston showing some data is reproduced in Figure 5.

Figure 5: Data on dinitrogen pentoxide decomposition (from Johnston).

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

$$\mathrm{N_2O_5} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_2} + \mathrm{NO_3} \tag{89}$$

$$\mathrm{NO_2} + \mathrm{NO_3} \xrightarrow{k_2} \mathrm{NO} + \mathrm{NO_2} + \mathrm{O_2} \tag{90}$$

$$\mathrm{NO} + \mathrm{NO_3} \xrightarrow{k_3} 2\mathrm{NO_2} \tag{91}$$

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

$$\frac{d[\mathrm{NO_2}]}{dt} = k_1[\mathrm{N_2O_5}] - k_{-1}[\mathrm{NO_2}][\mathrm{NO_3}] + 2k_3[\mathrm{NO}][\mathrm{NO_3}] \tag{92}$$

$$\frac{d[\mathrm{NO_3}]}{dt} = k_1[\mathrm{N_2O_5}] - (k_{-1} + k_2)[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO}][\mathrm{NO_3}] \tag{93}$$

Apply SSA to $\mathrm{NO_3}$:

$$\frac{d[\mathrm{NO_3}]}{dt} \overset{\text{SSA}}{\approx} 0 \tag{94}$$

$$[\mathrm{NO_3}] \overset{\text{SSA}}{\approx} \frac{k_1[\mathrm{N_2O_5}]}{(k_{-1} + k_2)[\mathrm{NO_2}] + k_3[\mathrm{NO}]} \tag{95}$$

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

$$\frac{d[\mathrm{NO_2}]}{dt} \overset{\text{SSA}}{\approx} k_1[\mathrm{N_2O_5}]\left\{1 - \frac{k_1[\mathrm{NO_2}] + -2k_3[\mathrm{NO}]}{(k_{-1} + k_2)[\mathrm{NO_2}] + k_3[\mathrm{NO}]}\right\} \tag{96}$$

$$\frac{d[\mathrm{NO_2}]}{dt} \overset{\text{SSA}}{\approx} k_1[\mathrm{N_2O_5}]\left\{\frac{k_2[\mathrm{NO_2}] + 3k_3[\mathrm{NO}]}{(k_{-1} + k_2)[\mathrm{NO_2}] + k_3[\mathrm{NO}]}\right\} \tag{97}$$

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

$$\frac{d[\mathrm{NO}]}{dt} = k_2[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO}][\mathrm{NO_3}] \overset{\text{SSA}}{\approx} 0 \tag{98}$$

$$[\mathrm{NO}] \overset{\text{SSA}}{\approx} \frac{k_2}{k_3}[\mathrm{NO_2}] \tag{99}$$

so

$$\frac{d[\mathrm{NO_2}]}{dt} \overset{\text{SSA}}{\approx} k_1[\mathrm{N_2O_5}]\left\{\frac{k_2[\mathrm{NO_2}] + 3k_2[\mathrm{NO_2}]}{(k_{-1} + 2k_2)[\mathrm{NO_2}]}\right\} \tag{100}$$

$$\frac{d[\mathrm{NO_2}]}{dt} \overset{\text{SSA}}{\approx} \frac{4k_1k_2}{k_{-1} + 2k_2}[\mathrm{N_2O_5}] \tag{101}$$

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.

2.8.3 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

$$\mathrm{Br_2} + \mathrm{N_3^-} \xrightarrow{\text{fast}} \mathrm{BrN_3} + \mathrm{Br^-} \tag{102}$$

$$\mathrm{BrN_3} + \mathrm{Br^-} \xrightleftharpoons{\mathrm{K_1}} \mathrm{Br_2N_3^-} \tag{103}$$

$$\mathrm{BrN_3} + \mathrm{N_3^-} \xrightarrow{\mathrm{k_1}} \mathrm{Br^-} + \mathrm{N_6} \tag{104}$$

$$\mathrm{N_6} \xrightarrow{\mathrm{k_3}} 3\mathrm{N_2} \tag{105}$$

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:

$$[\mathrm{N_6}] \overset{\mathrm{SSA}}{\approx} \frac{k_1}{k_3}[\mathrm{BrN_3}][\mathrm{N_3^-}] \tag{106}$$

$$\frac{d[\mathrm{N_2}]}{dt} = 3k_3[\mathrm{N_6}] \tag{107}$$

$$\overset{\mathrm{SSA}}{\approx} 3k_1[\mathrm{BrN_3}][\mathrm{N_3^-}] \tag{108}$$

The first reaction is "fast", so it is reasonable to regard the initially added bromine as converted completely to BrN_3 immediately. The BrN_3 can either be complexed by Br^- in step 103, or react to form product in step 104. The equilibrium gives us

$$[\mathrm{Br_2N_3^-}] \overset{\mathrm{REA}}{\approx} K_1[\mathrm{BrN_3}][\mathrm{Br^-}] \tag{109}$$

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.

$$\begin{aligned} M &= [\mathrm{BrN_3}] + [\mathrm{Br_2N_3^-}] && (110) \\ &\overset{\mathrm{REA}}{\approx} [\mathrm{BrN_3}] + K_1[\mathrm{BrN_3}][\mathrm{Br^-}] && (111) \\ &\overset{\mathrm{REA}}{\approx} [\mathrm{BrN_3}](1 + K_1[\mathrm{Br^-}]) && (112) \\ [\mathrm{BrN_3}] &\overset{\mathrm{REA}}{\approx} \frac{M}{1 + K_1[\mathrm{Br^-}]} && (113) \end{aligned}$$

Since M is only destroyed in step Eq. (104),

$$\begin{aligned} \frac{dM}{dt} &= -k_1[\mathrm{BrN_3}][\mathrm{N_3^-}] && (114) \\ &\overset{\mathrm{REA}}{\approx} -k_1[\mathrm{N_3^-}]\frac{M}{1 + K_1[\mathrm{Br^-}]} && (115) \end{aligned}$$

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

$$k_{\mathrm{eff}} = [\mathrm{N_3^-}]\frac{k_1}{1 + K_1[\mathrm{Br^-}]}. \tag{116}$$

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 $\mathrm{Br_3N_3^{2-}}$, and the $\mathrm{Br_2N_3^-}$ can react with azide to produce $\mathrm{N_6}$ 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.

3 Numerical Solutions to Rate Equations

The systems of coupled differential equations produced by even modestly complicated mechanisms are often difficult or impossible to solve analytically. The steady-state and equilibrium approximations sometimes can simplify them to tractable systems, but often they cannot, and even when they can it is not always clear that the approximations are good. A separate approach is to give up hope of obtaining analytic expressions for concentration as a function of time, but to solve the differential equations numerically. This approach just produces predicted curves of concentrations of all the species in the system, given the mechanism, the rate coefficients, and the initial conditions.

Several common motivations for numerical approaches are the following:

1. To handle hopelessly complicated mechanisms with many intermediates and many rate coefficients. In this case, it's the only game in town.
2. To verify the validity of SSA and similar approximations made in analytical approaches.
3. To get *C*-vs-*t* profiles, even for relatively simple mechanisms, for comparison to data.

3.1 Computational Methods

Two good references for numerical algorithms are C.W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice-Hall (Englewood Cliffs, NJ); 1971), and W.H. Press et al, *Numerical Recipes in [C or Fortran]*, 2nd edition, Cambridge University Press (NY; 1992).

The basic idea in all numerical approaches is that differential equations give you the *slope* on each concentration as a function of the concentrations. You can use that to trace out C vs. t. The simplest possible method is called Euler's method, and I will describe it briefly; an example is shown in Figure 6.

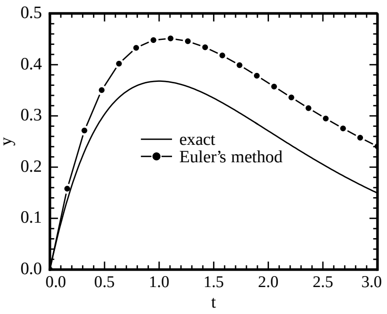

Figure 6: Euler's method solution for the equation $\frac{dy}{dt} = e^{-x}(1-x)$, with a step size of 0.158.

We describe the chemical system in terms of a vector of concentrations $\mathbf{y}$, and the mechanism gives us a corresponding vector of derivatives $\mathbf{y}'$.

Let us look at one particular component of $\mathbf{y}'$, $\frac{d[\mathrm{B}]}{dt}$:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] + (k_{-1} + k_2[\mathrm{C}])[\mathrm{B}] + \cdots \tag{117}$$

$$= f(\mathbf{y}). \tag{118}$$

At $t = 0$, we have $\mathbf{y} = \mathbf{y}_0$, $\mathbf{y}' = \mathbf{y}'_0$.

Take a small step in t, called h. Assume that the step is small enough that the concentrations change linearly during it. Then

$$\mathbf{y}(h) = \mathbf{y}(0) + h\mathbf{y}'(0). \tag{119}$$

For the next step, take

$$\mathbf{y}(2h) = \mathbf{y}(h) + h\mathbf{y}'(h), \tag{120}$$

and so on.

I do *not* recommend this technique for any real problems. But it gives you the idea. Better methods calculate the slope halfway between the steps, or fit parabolas instead of straight lines, or vary the stepsizes to fit the problem . . . (see the references given above for details.)

A problem that often occurs in kinetics is that rate constants of quite different magnitudes appear in the problems. For example, in the simple mechanism

$$\mathrm{A} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{B} \tag{121}$$

$$\mathrm{B} \xrightarrow{\mathrm{k}_2} \mathrm{C} \tag{122}$$

if $k_{-1} \gg k_2$, then even *after* the equilibrium is established, the numerical routine must keep taking small steps because $1/k_{-1}$ is small. The required small time steps make the problem slow (= expensive). This is called “stiffness”. Many realistic kinetic systems, including ones where the rapid equilibrium or SS approximations are useful, are stiff.

The Euler method I described above, and the Runge-Kutta method described in Espenson, both are susceptible to stiffness. More sophisticated numerical methods are required. Several different ones are available, but the best developed ones are descendants of the modified ”predictor-corrector” one developed by Gear.

3.2 Simulation programs

Several different programs are available for performing numerical solutions of kinetic systems. The ones I have found useful are listed below.

Kinsim (Barshop et al., *Biochem. J.* **258**, 381 (1989); available at `http://wuarchive.wustl.edu/packages/kinsim/`) Kinsim is a very popular Gear-type simulator. It includes a fitting program (`Fitsim`) that can adjust the rate coefficients to fit real data. Both `Kinsim` and `Fitsim` are installed on the Windows computers in the graduate computer laboratory. See the handout for a brief introduction to its use; a complete manual is available at the web site listed above.

React (Written by Mike Whitbeck of Lawrence Livermore National Laboratory). `React` is similar to Kinsim, though I have found it a little less reliable. The source code is not available, but compiled versions for DOS, Macintosh, and OS/2 are available at the Computational Chemistry List server at OSC: `ftp://ccl.osc.edu/pub/chemistry/software/MAC/react/`, or `ftp://ccl.osc.edu/pub/chemistry/software/MS-DOS/react/`.)

Acuchem This is an old-style DOS program described in Braun et al., *Int. J. Chem. Kin.* **20**, 51 (1988). It has somewhat more convenient data entry than the previous two, but provides output is less convenient forms. It is very reliable. Copies are available from me on disk.

CKS This program uses a different approach than the previous ones. It is a "stochastic simulator"; it does a sort of Monte Carlo simulation of a very small volume within the chemical system that contains typically a few thousand molecules, and it does not treat the system with differential equations at all. `CKS` is basically a repackaging of the program described by Bunker et al. in *Combustion and Flame* **22**, 375 (1974); for a thorough analysis of the stochastic method, see Gillespie (*J. Computational Phys.* **22**, 403 (1976)). For most kinds of mechanisms it is not competitive with the Gear integrators for speed (statements in its documentation to the contrary notwithstanding). It is especially poor at handling systems with fast equilibria. Also, because of its stochastic nature the output data of concentration vs. time have "noise" on them. However, it is a very nicely designed program, it runs on Windows, Mac, and OS/2 computers, and it is probably the easiest to use of all the programs listed. It is available at `http://www.almaden.ibm.com/st/msim/`.

CHEMKIN This is the heavy-duty, no-holds-barred program system developed at Sandia National Laboratory for simulating reactions (especially combustion) in flowing, nonisothermal systems with hundreds of species and perhaps thousands of elementary reactions. It is a Gear integrator. It is now distributed by a commercial firm, though it is available at modest cost to universities. Information about ordering it is at `http://www.reactiondesign.com/`.

4 Construction of Candidate Mechanisms from Rate Laws

4.1 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.

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.

Here we have

$$A \longrightarrow X_2 \longrightarrow P. \tag{123}$$

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.

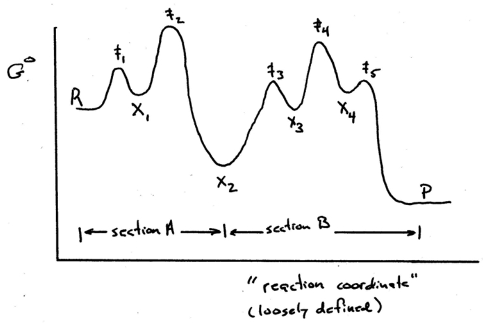

Figure 7: Schematic free energy diagram for sequential 1st-order system with 4 intermediates, $A \rightarrow X, \rightarrow X_2 \rightarrow X_3 \rightarrow X_4 \rightarrow P$

In Figure 7, 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).

4.2 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 2.8.2,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2, \tag{124}$$

with rate law

$$\frac{d[N_2O_5]}{dt} = k[N_2O_5], \tag{125}$$

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

In the aqueous redox reaction

$$Tl^{3+} + Hg_2^{2+} \longrightarrow Tl^{+} + 2Hg^{2+}, \tag{126}$$

$$\text{rate} = k\frac{[Tl^{3+}][Hg_2^{2+}]}{[Hg^{2+}]}. \tag{127}$$

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:

$$2(Mn^{III}MG)^{+} + S_2O_4^{2-} \longrightarrow 2(Mn^{II}MG) + 2SO_2, \tag{128}$$

where MG is the protein myoglobin, has the rate law

$$\text{rate} = k[(Mn^{III}MG)^{+}][S_2O_4^{2-}]^{\frac{1}{2}}, \tag{129}$$

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.

$$3I^{-} + H_2O_2 + 2H^{+} \longrightarrow I_3^{-} + 2H_2O \tag{130}$$

$$\frac{d[I_3^{-}]}{dt} = k_a[I^{-}][H_2O_2] + k_b[I^{-}][H_2O_2][H^{+}] \tag{131}$$

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 $[\mathrm{H}^+]$. There are two pathways, plain and catalyzed, with compositions in the TS of $(\mathrm{H_2O_2I})^-$ and $\mathrm{H_3O_2I}$.

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

$$\mathrm{A} + \mathrm{B} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{C} \tag{132}$$

$$\mathrm{C} + \mathrm{A} \xrightarrow{\mathrm{k}_2} \mathrm{D} \tag{133}$$

$$\mathrm{C} \xrightarrow{\mathrm{k}_3} \mathrm{D} \tag{134}$$

Applying SSA to C,

$$0 \overset{\mathrm{SSA}}{\approx} \frac{d[\mathrm{C}]}{dt} = k_1[\mathrm{A}][\mathrm{B}] - (k_{-1} + k_3 + k_2[\mathrm{A}])[\mathrm{C}] \tag{135}$$

so

$$[\mathrm{C}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{A}][\mathrm{B}]}{k_{-1} + k_3 + k_2[\mathrm{A}]} \tag{136}$$

Now

$$\frac{d[\mathrm{D}]}{dt} = k_2[\mathrm{A}][\mathrm{C}] + k_3[\mathrm{C}] \tag{137}$$

$$= \frac{k_1 k_2 [\mathrm{A}]^2[\mathrm{B}]}{k_{-1} + k_3 + k_2[\mathrm{A}]} + \frac{k_1 k_3 [\mathrm{A}][\mathrm{B}]}{k_{-1} + k_3 + k_2[\mathrm{A}]} \tag{138}$$

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

$$\text{rate} = \left(\frac{\mathrm{k}_1\mathrm{k}_2}{\mathrm{k}_{-1} + \mathrm{k}_3}\right)[\mathrm{A}]^2[\mathrm{B}] + \left(\frac{\mathrm{k}_1\mathrm{k}_3}{\mathrm{k}_{-1} + \mathrm{k}_3}\right)[\mathrm{A}][\mathrm{B}] \tag{139}$$

and we correctly interpret that there are two important transition states with compositions $\mathrm{A_2B}$ and AB.

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

$$\text{rate} = k_1[\mathrm{A}][\mathrm{B}] + \frac{k_1 k_3}{k_2}[\mathrm{B}] \tag{140}$$

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

$$k_2 \cdot \text{rate} = k_1 k_2 [\mathrm{A}][\mathrm{B}] + k_1 k_3 [\mathrm{B}] \tag{141}$$

$$= k_1[\mathrm{B}](k_2[\mathrm{A}] + k_3) \tag{142}$$

$$\approx k_1[\mathrm{B}]k_2[\mathrm{A}] \qquad \text{(from large [A] assumption)} \tag{143}$$

$$\text{rate} = k_1[\mathrm{A}][\mathrm{B}] \tag{144}$$

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.

$$2\mathrm{Fe}^{2+} + \mathrm{Tl}^{3+} \to 2\mathrm{Fe}^{3+} + \mathrm{Tl}^{+} \tag{145}$$

$$-\frac{d[\mathrm{Tl}^{3+}]}{dt} = \frac{k[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{[\mathrm{Fe}^{2+}] + k'[\mathrm{Fe}^{3+}]} \tag{146}$$

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,

$$\text{rate} = \frac{k}{k'}\frac{[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{[\mathrm{Fe}^{3+}]}. \tag{147}$$

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:

$$\mathrm{Fe}^{2+} + \mathrm{Tl}^{3+} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{Fe}^{3+} + \mathrm{Tl}^{2+} \tag{148}$$

$$\mathrm{Tl}^{2+} + \mathrm{Fe}^{2+} \xrightarrow{\mathrm{k}_2} \mathrm{Fe}^{3+} + \mathrm{Tl}^{+} \tag{149}$$

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

$$\frac{d[\mathrm{Tl}^{2+}]}{dt} = k_1[\mathrm{Fe}^{2+}][\mathrm{Tl}^{3+}] - [\mathrm{Tl}^{2+}](k_{-1}[\mathrm{Fe}^{3+}] + k_2[\mathrm{Fe}^{2+}]) \tag{150}$$

so

$$[\mathrm{Tl}^{2+}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{Fe}^{2+}][\mathrm{Tl}^{3+}]}{k_{-1}[\mathrm{Fe}^{3+}] + k_2[\mathrm{Fe}^{3+}]} = \frac{k[\mathrm{Fe}^{2+}][\mathrm{Tl}^{3+}]}{[\mathrm{Fe}^{3+}] + k^1[\mathrm{Fe}^{2+}]} \tag{151}$$

$$\text{rate} = k_2[\mathrm{Tl}^{2+}][\mathrm{Fe}^{2+}] = \frac{k_1k_2[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{k_{-1}[\mathrm{Fe}^{3+}] + k_2[\mathrm{Fe}^{2+}]} \tag{152}$$

$$\text{rate} = \frac{k[\mathrm{Fe}^{2+}]^2[\mathrm{Tl}^{3+}]}{k'[\mathrm{Fe}^{3+}] + [\mathrm{Fe}^{2+}]} \tag{153}$$

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.

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

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

$$2V^{3+} + 2Hg^{2+} \longrightarrow 2V^{IV} + Hg_2^{2+} \tag{154}$$

The observed rate law is

$$-\frac{d[V^{3+}]}{dt} = \frac{k[V^{3+}]^2[Hg^{2+}]}{k'[V^{IV}] + [V^{3+}]}. \tag{155}$$

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:

$$V^{3+} + Hg^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V^{IV} + Hg^{+} \tag{156}$$

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.

$$Hg^{+} + V^{3+} \xrightarrow{k_2} V^{IV} + Hg^{0} \tag{157}$$

$$Hg^{0} + Hg^{2+} \xrightarrow{k_3} Hg_2^{2+} \tag{158}$$

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

$$\frac{d[Hg^{+}]}{dt} = k_1[V^{3+}][Hg^{2+}] - k_{-1}[V^{IV}][Hg^{+}] - k_2[V^{3+}][Hg^{+}] \tag{159}$$

$$[Hg^{+}] \overset{\text{SSA}}{\approx} \frac{k_1[V^{3+}][Hg^{2+}]}{k_{-1}[V^{IV}] + k_2[V^{3+}]} \tag{160}$$

$$-\frac{d[V^{3+}]}{dt} \overset{\text{SSA}}{\approx} k_1[V^{3+}][Hg^{2+}] - k_{-1}[V^{IV}][Hg^{+}] + k_2[V^{3+}][Hg^{+}] \tag{161}$$

$$= k_1[V^{3+}][Hg^{2+}] + [Hg^{+}](k_2[V^{3+}] - k_{-1}[V^{IV}]) \tag{162}$$

$$= k_1[V^{3+}][Hg^{2+}] + \left(\frac{k_1[V^{3+}][Hg^{2+}]}{k_{-1}[V^{IV}] + k_2[V^{3+}]}\right)(k_2[V^{3+}] - k_{-1}[V^{IV}]) \tag{163}$$

$$= k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}]\left(1 + \frac{\left(k_2[\mathrm{V}^{3+}] - k_{-1}[\mathrm{V}^{\mathrm{IV}}]\right)}{k_{-1}[\mathrm{V}^{\mathrm{IV}}] + k_2[\mathrm{V}^{3+}]}\right) \tag{164}$$

$$= k_1[\mathrm{V}^{3+}][\mathrm{Hg}^{2+}]\left(\frac{2k_2[\mathrm{V}^{3+}]}{k_{-1}[\mathrm{V}^{\mathrm{IV}}] + k_2[\mathrm{V}^{3+}]}\right) \tag{165}$$

$$= \frac{2k_1[\mathrm{V}^{3+}]^2[\mathrm{Hg}^{2+}]}{\frac{k_{-1}}{k_2}[\mathrm{V}^{\mathrm{IV}}] + [\mathrm{V}^{3+}]} \tag{166}$$

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.

4.4 Half-integral orders

These are common both in dissociative equilibrium reactions and in free-radical chain reactions (eg. $\mathrm{H}_2 + \mathrm{Br}_2$.)

4.4.1 Dissociative equilibrium

The dissociative equilibrium case is

$$\mathrm{A} \quad \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \quad 2\mathrm{B} \tag{167}$$

$$2(\mathrm{B} + \mathrm{C} \quad \xrightarrow{\mathrm{k}_2} \quad \mathrm{D}), \tag{168}$$

which gives the overall reaction

$$\mathrm{A} + 2\mathrm{C} \longrightarrow 2\mathrm{D}. \tag{169}$$

If the $\mathrm{A} \rightleftharpoons \mathrm{B}$ equilibrium is rapid,

$$K_{\mathrm{eq}} = \frac{[\mathrm{B}]^2_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \tag{170}$$

$$[\mathrm{B}]_{\mathrm{eq}} = K_{\mathrm{eq}}^{\frac{1}{2}}[\mathrm{A}]^{\frac{1}{2}} \tag{171}$$

$$\frac{d[\mathrm{D}]}{dt} = k_2[\mathrm{B}][\mathrm{C}] \tag{172}$$

$$= K_{\mathrm{eq}}^{\frac{1}{2}}k_2[\mathrm{A}]^{\frac{1}{2}}[\mathrm{C}] \tag{173}$$

4.4.2 Radical reactions

For radical chain mechanisms, there is a set of "mechanistic rules" similar to those we have used, called the Goldfinger-Letort-Niclause notes. They consider whether the chain-propagating reactions are first or second order, etc. See Laidler for a discussion.

A simple example of a radical half-integral reaction is acetaldehyde thermal decomposition:

$$\mathrm{CH_3CHO} \xrightarrow{k_1} \mathrm{CH_3} + \mathrm{CHO} \qquad \text{initiation} \tag{174}$$

$$\mathrm{CH_3} + \mathrm{CH_3CHO} \xrightarrow{k_2} \mathrm{CH_4} + \mathrm{CH_3CO} \qquad \text{propagation} \tag{175}$$

$$\mathrm{CH_3CO} \xrightarrow{k_3} \mathrm{CH_3} + \mathrm{CO} \qquad \text{propagation} \tag{176}$$

$$2\mathrm{CH_3} \xrightarrow{k_4} \mathrm{C_2H_6} \qquad \text{termination} \tag{177}$$

Applying the SSA to CH_3 and CH_3CO and adding the $d[]/dt = 0$ equations together (a common trick in radical mechanisms) we get

$$[\mathrm{CH_3}] = \left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [\mathrm{CH_3CHO}]^{\frac{1}{2}}. \tag{178}$$

Since

$$\frac{d[\mathrm{CH_4}]}{dt} = k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}], \tag{179}$$

the overall reaction is 3/2 order in CH_3CHO. Laidler gives a good discussion of radical mechanisms and the conditions under which various orders appear.

5 Enzyme Catalysis

A catalyst is a substance that speeds up a reaction without itself being consumed. It speeds up a reaction by providing a new mechanistic path to products with a higher rate than the original, uncatalyzed pathway.

5.1 Basic mechanism

An important class of biological catalysts is the enzymes. These are proteins which typically act as very specific catalysts. The reactant whose transformation is catalyzed by the enzyme is called the substrate.

The simplest ("Briggs-Haldane") mechanism is

$$\mathrm{S} + \mathrm{E} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{ES} \tag{180}$$

$$\mathrm{ES} \xrightarrow{\mathrm{k}_2} \mathrm{P} + \mathrm{E} \tag{181}$$

Applying the SSA to [ES] we obtain

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - (k_{-1} + k_2)[\mathrm{ES}] \tag{182}$$

$$[\mathrm{ES}] \overset{\mathrm{SSA}}{\approx} \frac{k_1[\mathrm{E}][\mathrm{S}]}{k_{-1} + k_2} \tag{183}$$

Since [E] is usually small, and a decent fraction of the enzyme may be complexed as ES, it is useful to write

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}] = [\mathrm{E}]\left(1 + \frac{k_1[\mathrm{S}]}{k_{-1} + k_2}\right), \tag{184}$$

so that

$$[\mathrm{E}] = \frac{(k_{-1} + k_2)[\mathrm{E}]_0}{k_{-1} + k_2 + k_1[\mathrm{S}]}. \tag{185}$$

Then

$$[\mathrm{ES}] = \frac{k_1[\mathrm{S}]}{k_{-1} + k_2}\,\frac{(k_{-1} + k_2)[\mathrm{E}]_0}{k_{-1} + k_2 + k_1[\mathrm{S}]} \tag{186}$$

$$= \frac{k_1[\mathrm{S}][\mathrm{E}]_0}{k_{-1} + k_2 + k_1[\mathrm{S}]}. \tag{187}$$

The reaction rate is

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] \overset{\mathrm{SSA}}{\approx} \frac{k_1 k_2 [\mathrm{S}][\mathrm{E}]_0}{k_{-1} + k_2 + k_1[\mathrm{S}]} \tag{188}$$

$$= \frac{k_2[\mathrm{E}]_0}{1 + \frac{k_{-1}+k_2}{k_1[\mathrm{S}]}} \tag{189}$$

$$\frac{d[\mathrm{P}]}{dt} = \frac{v_s}{1 + \frac{K_M}{[\mathrm{S}]}} = \frac{v_s[\mathrm{S}]}{K_M + [\mathrm{S}]}, \tag{190}$$

Eq. (190) is called the Michaelis-Menten equation. $K_\mathrm{M} = \frac{k_{-1}+k_2}{k_1}$ is the Michaelis constant. It has units of concentration and gives the concentration of S at which the reaction rate has reached half its maximum value (and approximately half the enzyme is tied up in ES.)

At small [S], $K_\mathrm{M}/[\mathrm{S}] \gg 1$, so

$$\frac{d[\mathrm{P}]}{dt} \sim \frac{v_s}{K_\mathrm{M}}[\mathrm{S}] \tag{191}$$

and the kinetics looks 1st order in S. At large [S], $d[\mathrm{P}]/dt$ is independent of [S]. The enzyme is then said to be saturated, and the observed rate is v_S.

5.2 Data analysis

Experiments are often carried out with the initial rates approach; they are done on a timescale slow compared to establishment of the steady state but fast compared to the depletion of S, so that rates of product formation $d[\mathrm{P}]/dt$ as functions of [S] can be determined.

Several "standard" plots are used in analysis of enzyme kinetic data, and are illustrated in Figure 8. The simplest is the Michaelis-Menten plot, shown in the top panel. For quantitative analysis (determination of K_M and v_S,) the Lineweaver-Burk and Eadie-Hofstee plots are used more often. Of these three, the E-H plot gives the most precise determination of K_M. It is based on the rewritten form of the M-M equation

$$\frac{1}{[\mathrm{S}]}\frac{d[\mathrm{P}]}{dt} = -\frac{1}{K_\mathrm{M}}\frac{d[\mathrm{P}]}{dt} + \frac{v_s}{K_\mathrm{M}}. \tag{192}$$

Often $[\mathrm{E}]_0$ is not known, because it is difficult to obtain pure enzymes. If it is known, k_2 can be determined from the experimental value of v_s.

5.3 Transient state kinetics

Whether $[\mathrm{E}]_0$ is known or not, these "steady-state" experiments do not allow us to find values for k_1 or k_{-1}. To do that, we need to do kinetics in the transient phase before the steady-state condition on ES is satisfied.

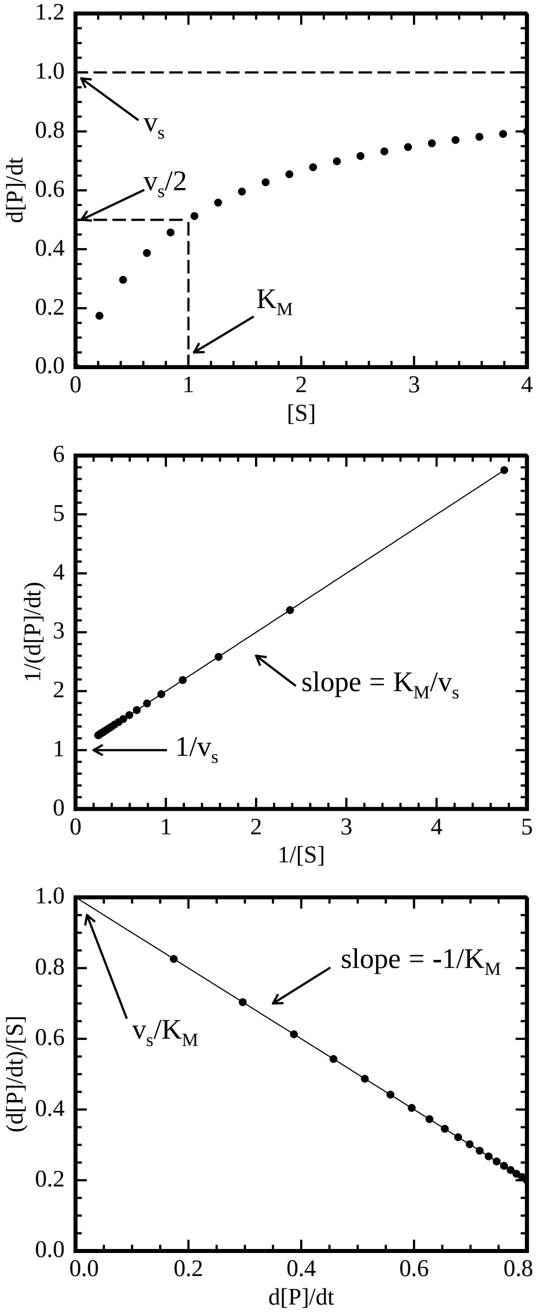

Figure 8: Three common enzyme kinetic plots. The three panels (top to bottom) show Michaelis-Menten, Lineweaver-Burk, and Eadie-Hofstee plots.

Let's find a complete solution for [ES] and [P] for times short enough that $[\mathrm{S}] \approx [\mathrm{S}]_0$.

$$\begin{aligned} \frac{d[\mathrm{ES}]}{dt} &= k_1[\mathrm{E}][\mathrm{S}] - (k_{-1} + k_2)[\mathrm{ES}] && (193) \\ &= -[\mathrm{ES}](k_1[\mathrm{S}] + k_{-1} + k_2) + k_1[\mathrm{S}][\mathrm{E}]_0. && (194) \end{aligned}$$

Now use

$$[\mathrm{S}] \approx [\mathrm{S}]_0 \tag{195}$$

and define

$$\begin{aligned} \sigma &= k_1[\mathrm{S}]_0 + k_{-1} + k_2 && (196) \\ b &= k_1[\mathrm{S}]_0[\mathrm{E}]_0. && (197) \end{aligned}$$

Now

$$\frac{d[\mathrm{ES}]}{dt} = -\sigma[\mathrm{ES}] + b \tag{198}$$

This is a separable DE with solution

$$[\mathrm{ES}] = \frac{b - Ce^{-\sigma t}}{\sigma}, \tag{199}$$

and because $[\mathrm{ES}](t = 0) = 0$, $C = b$. Then

$$\begin{aligned} [\mathrm{ES}] &= \frac{b}{\sigma}(1 - e^{-\sigma t}) && (200) \\ \frac{d[\mathrm{P}]}{dt} &= k_2[\mathrm{ES}] = \frac{k_2 b}{\sigma}(1 - e^{-\sigma t}) && (201) \\ [\mathrm{P}](t) &= \frac{k_2 b}{\sigma} \int 1 - e^{-\sigma t} dt && (202) \\ &= \frac{k_2 b}{\sigma} \left(t + \frac{1}{\sigma} e^{-\sigma t} + C \right) && (203) \end{aligned}$$

Since $[\mathrm{P}](t = 0) = 0$, $C = -1/\sigma$, and we have

$$[\mathrm{P}](t) = \frac{k_2 b}{\sigma} \left(t + \frac{1}{\sigma}(e^{-\sigma t} - 1) \right) \tag{204}$$

For $t \gg 1/\sigma$ (but small enough that $[\mathrm{S}] \approx [\mathrm{S}]_0$), a plot of [P] vs. t will be a line with slope $k_2 b/\sigma$ and x-intercept $t = \frac{1}{\sigma}$, as shown in Figure 9. If we measure σ at several different $[\mathrm{S}]_0$, we can make a plot of σ against $[\mathrm{S}]_0$, which will have slope k_1 and y-intercept $k_{-1} + k_2$ as shown in the lower panel of Figure 9. If k_2 can be evaluated from a knowledge of $[\mathrm{E}]_0$ and the steady-state kinetics, then we have enough information to determine all the elementary rate coefficients in the Briggs-Haldane mechanism.

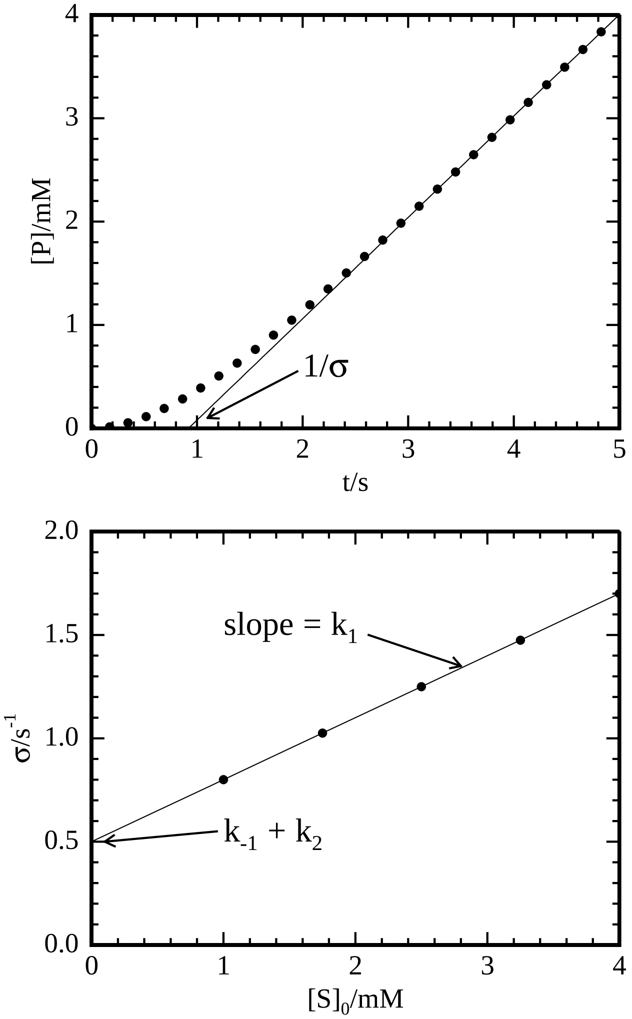

Figure 9: Enzyme kinetics in the transient region.

6 Experimental Techniques

6.1 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.

6.2 Stable reactants, slow to medium time scales

6.2.1 Batch mixing

This is kinetics on classical stir-in-a-pot reactions. It works for $\tau_{\text{min}} \gtrsim 10\,\text{s}$. 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.

6.2.2 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 10.

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.

6.3 Near-equilibrium methods for fast reactions

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

Figure 10: Schematic of stopped-flow apparatus

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

Let reaction come to equilibrium, with concentrations A_e, B_e, Z_e for $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{Z}$. 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: $\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Z}$

$$k_1 A_e B_e = k_{-1} Z_e \tag{205}$$

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}][\mathrm{B}] + k_{-1}[\mathrm{Z}] \tag{206}$$

Write

$$[\mathrm{A}] = A_e - \delta, [\mathrm{B}] = B_e - \delta, [\mathrm{Z}] = Z_e + \delta \tag{207}$$

$$\frac{d[\mathrm{A}]}{dt} = -\frac{d\delta}{dt} = -k_1(A_e - \delta)(B_e - \delta) + k_{-1}(Z_e + \delta) \tag{208}$$

$$-\frac{d\delta}{dt} = -k_1(A_e B_e - (A_e + B_e)\delta + \delta^2) + k_{-1} Z_e + k_{-1}\delta \tag{209}$$

$$-\frac{d\delta}{dt} = \delta(k_1(A_e + B_e) + k_{-1} - k_1\delta) \underbrace{-k_1 A_e B_e + k_{-1} Z_e}_{=0} \tag{210}$$

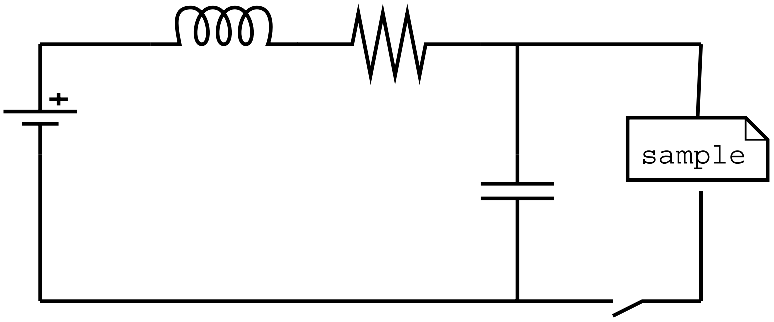

Figure 11: Schematic of T-jump apparatus

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

$$\frac{d\delta}{dt} \approx -(k_1(A_e + B_e) + k_{-1})\delta, \tag{211}$$

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 electrical current. Figure 11 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.)

6.3.2 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 ^{1}H 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, as illustrated in Figure 12. An analysis of the lineshape can therefore be used to determine the rate of exchange.

Figure 12: NMR lineshapes (from Espenson).

The "experimental timescale" is given roughly by $1/\Delta\nu$, where $\Delta\nu$ is the difference in asborption frequencies in the absence of exchange. (Alternatively, in modern pulse nmr, it is related to T_2, the spin-spin relaxation time). 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 $K_{\mathrm{eq}} = 0.5$.) Most new nmr spectrometers contain canned software to do these lineshape analyses.

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

$$\mathrm{CH_3CH_2OH^a + H_2^bO \rightleftharpoons CH_3CH_2OH^b + H^aOH^b} \qquad (212)$$

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.

6.4 Flash Photolysis

Flash photolysis is the main techniques 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:

$$\mathrm{P} \xrightarrow{\mathrm{hv}} \mathrm{A}\ (\text{+ other stuff}) \tag{213}$$

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{products} \tag{214}$$

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

$$\mathrm{SO_2} \xrightarrow{\mathrm{193nm, 10ns}} \mathrm{SO} + \mathrm{O}(^3P) \tag{215}$$

$$\mathrm{O}(^3P) + \mathrm{C_2H_2} \longrightarrow \mathrm{HCCHO}^* \tag{216}$$

$$\mathrm{HCCHO}^* \longrightarrow \mathrm{H} + \mathrm{HCCO} \tag{217}$$

$$\mathrm{HCCHO}^* \longrightarrow \mathrm{CH_2} + \mathrm{CO} \tag{218}$$

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

6.5 Discharge Flow Experiments

Discharge flow experiments use a steady electric discharge to produce reactants, 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. This is a very popular method for studying reactions of radical and ionic species.

Figure 13:

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 techniques.

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:

$$
\begin{aligned}
H_2 &\xrightarrow{\mu\text{wave}} 2H && && (219)\\
H + NO_2 &\longrightarrow OH + NO && \text{fast,} && (220)\\
F_2 &\xrightarrow{\mu\text{wave}} 2F && && (221)\\
F + CH_4 &\longrightarrow CH_3 + HF && \text{fast,} && (222)\\
OH + CH_3 &\longrightarrow H_2O + CH_2 && \text{(plus other channels)} && (223)
\end{aligned}
$$

They detected detect OH at different distances along the flow tube with fluorescence.

An important technique in flow-tube experiments is the ability to *titrate* the reactive species with fast reactions.

$$\begin{aligned}
O_2 &\xrightarrow{\mu\text{wave}} 2O && (224)\\
O + NO_2 &\longrightarrow NO + O_2 && (225)\\
O + NO &\longrightarrow NO_2^* && (226)\\
NO_2^* &\xrightarrow{-h\nu} NO_2. && (227)
\end{aligned}$$

By calibrating the flow of NO_2, and watching the green fluorescence from NO_2^*, one can accurately determine [O] at different points along the tube.

6.6 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 (700-2500k), and is nearly the only technique for gas phase reactions above $\approx 1400K$. Many of the rate coefficients needed in Kinsim-like models of hydrocarbon combustion have been measured this way.

Figure 14:

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.

7 Temperature Dependence of Rates

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

$$k = Ae^{-E_a/RT} \tag{228}$$

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. We shall find the assumptions underlying the Arrhenius equation shortly. In the meantime, I want to point out that the parameters A and E_a should be regarded as empirical quantities with the *definitions*

$$E_a(T) = -R\frac{d(\ln k)}{d(1/T)} \tag{229}$$

$$= RT^2\frac{d(\ln k)}{dT} \tag{230}$$

$$A(T) = k(T)/\exp(-E_a(T)/RT) \tag{231}$$

The necessary function $k(T)$ can be obtained either from experiment or from some theory, but A and E_a should not be regarded as having underlying physical significance in most cases. For elementary reactions, some theories of kinetics do ascribe precise meanings to them.

Figure 15 shows the behavior predicted by the Arrhenius equation for the two common plots, k vs. T and $\ln(k)$ vs. $1/T$.

Figure 15: Two plots of rate coefficients for a reaction with $A = 10^{10}$ $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ and $E_a = 20$ kJ/mol.

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 modem 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 15.

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 16.

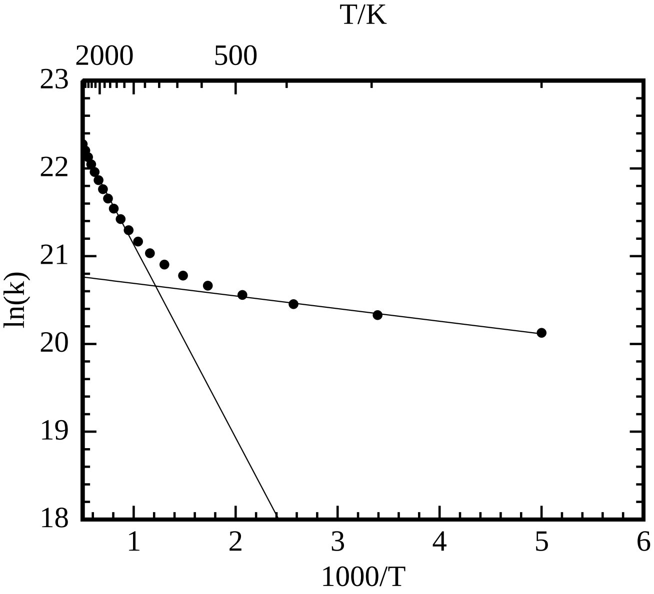

Figure 16: "Arrhenius plot" for a reaction that does not follow simple Arrhenius behavior.

Data that show curvature on Arrhenius plots are most often fitted by the equation

$$k(T) = AT^m e^{-E_b/RT}, \tag{232}$$

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.

7.1 Hard-sphere collisions

Consider a very simple hard-sphere model of a bimolecular reaction:

Figure 17:

Kinetic theory of gases gives a formula for the number of A-B collisions per unit time:

$$Z_{\mathrm{AB}} = \pi(r_{\mathrm{A}} + r_{\mathrm{B}})^2 u n_{\mathrm{A}} n_{\mathrm{B}}, \tag{233}$$

where $\pi(r_{\mathrm{A}} + r_{\mathrm{B}})^2$ is the collision cross section (units m^2), u is the relative speed $|\mathbf{v}_{\mathrm{A}} - \mathbf{v}_{\mathrm{B}}|$ of the colliding molecules (units $\mathrm{m/s}$), and n_{A} and n_{B} are the densities of the A and B molecules (units m^{-3}.).

Z_{AB} has units $\mathrm{m}^3\mathrm{s}^{-1}$, actually collisions/ m^3s.

Some fraction of those collisions will result in reaction, so the number of reactions per second per m^3 is

$$\text{Rate} = P_{\mathrm{r}} \pi(r_A + r_B)^2 u n_A n_B, \tag{234}$$

where P_{r} is the probability of reaction upon each hard-sphere collision.

An elementary bimolecular reaction has rate law

$$\text{Rate} = k n_A n_B, \tag{235}$$

so

$$k = P_{\mathrm{r}} \pi(r_A + r_B)^2 u = \sigma u, \tag{236}$$

where σ is the *reaction cross section*.

P_{r} might depend on many things in real reactions: collision velocity, orientation of molecules, internal energy of molecules, etc. If we assume in this hard-sphere case that P_r only depends on the relative velocity of the colliding spheres, we write

$$k = u\sigma(u). \tag{237}$$

If we have a distribution of relative velocities rather than a single sharp one, we must average over the velocity distribution $f(u)du$:

$$k = \int_0^\infty u\sigma(u)f(u)du \tag{238}$$

(Here $f(u)du$ is a probability, so $f(u)$ is a probability density; $\int_0^\infty f(u)\,du = 1$.)

Now we can evaluate $k's$ by inserting different functions for $\sigma(u)$ and $f(u)$.

The simplest possible case is high-energy scattering of hard spheres at a specified collision velocity (perhaps Ne-He collisions in a high energy molecular beam experiment).

$$\sigma(u) = \sigma_0 = \pi(r_A + r_B)^2 \tag{239}$$

(meaning $P_\mathrm{r} = 1$ always)

$$f(u) = \delta(u - u_0) \tag{240}$$

Then

$$k = \int_0^\infty u\sigma_0\delta(u - u_0)du = \sigma_0 u_0 \tag{241}$$

If $\sigma(u)$ depends on velocity (the "effective size" changes with velocity) but the relative speed distribution is still sharp, we get

$$k = \int_0^\infty u\sigma(u)\delta(u - u_0)du = \sigma(u_0)u_0 \tag{242}$$

Generally, reactions do not occur with well-defined collision velocities, but with well-defined temperatures. We then need the Maxwell-Boltzmann distribution of relative speeds:

$$f(u) = 4\pi\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} u^2 e^{-\frac{\mu u^2}{2k_B T}} \tag{243}$$

where μ is the reduced mass, $\frac{m_A m_B}{m_A + m_B}$, and k_B is Boltzmann's constant.

With that relative velocity distribution,

$$k(T) = 4\pi\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \int_0^\infty \sigma(u)u^3 e^{-\frac{\mu u^2}{2k_B T}} du \tag{244}$$

Figure 18:

Change variables to collision *energy*

$$\varepsilon_t = \frac{1}{2}\mu u^2 \tag{245}$$

$$d\varepsilon_t = \mu u \, du \tag{246}$$

Multiply (inside) and divide (outside) by $\mu^2/2$

$$k(T) = \frac{8\pi}{\mu^2}\left(\frac{\mu}{2\pi k_B T}\right)^{3/2}\int_0^\infty \frac{\mu u^2}{2}\sigma(\varepsilon_t)e^{-\frac{\mu u^2}{2k_B T}}\mu u du \tag{247}$$

$$k(T) = \frac{8\pi}{\mu^2}\left(\frac{\mu}{2\pi k_B T}\right)^{3/2}\int_0^\infty \varepsilon_t\sigma(\varepsilon_t)e^{-\varepsilon_t/k_B T}d\varepsilon_t \tag{248}$$

We now have the cross section written as a function of collision energy rather than velocity, but it contains the same information.

This is the collision theory expression for the second order elementary rate coefficient. We have assumed that the only factor affecting whether a collision results in reaction is collision energy. What might be a reasonable form for $\sigma(\varepsilon_t)$? In many reactions we expect a "threshold energy"; there's an "energy hill" which must be surmounted.

So reasonable $\sigma(\varepsilon_t)$ might look like the ones illustrated on the next page.

I want to calculate the $k(T)$ expected for several plausible model functions $\sigma(\varepsilon_t)$.

1) Every hard-sphere collision reacts.

$$\sigma(\varepsilon_t) = \sigma_0 = \pi d^2 \tag{249}$$

$$k(T) = \frac{8\pi}{\mu^2}\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \sigma_0 \int_0^\infty \varepsilon_t e^{-\varepsilon_t/k_B T} d\varepsilon_t \tag{250}$$

Integrate by parts to get

$$k(T) = \frac{8\pi}{\mu^2}\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \sigma_0 (k_B T)^2 = \left(\frac{8k_8 T}{\pi\mu}\right)^{1/2} \sigma_0 = \bar{u}\sigma_0 \tag{251}$$

This simple model recovers the hard-sphere collision frequency we began with.

T dependence is predicted to be

$$k(T) = AT^{1/2}. \tag{252}$$

Very few reactions are well described by this model.

A better model might assign a higher probability of reaction to a head-on collision than to a glancing one. A simple application of this idea results in the "line of centers" model.

8 Simple rate coefficient calculations

I want to calculate the $k(T)$ expected for several plausible model functions $\sigma(\varepsilon_t)$.

8.1 Every hard-sphere collision reacts

$$\sigma(\varepsilon_t) = \sigma_0 = \pi d^2 \tag{253}$$

$$k(T) = \frac{8\pi}{\mu^2}\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \sigma_0 \int_0^\infty \varepsilon_t e^{-\varepsilon_t/k_B T} d\varepsilon_t \tag{254}$$

Integrate by parts to get

$$k(T) = \frac{8\pi}{\mu^2}\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \sigma_0 (k_B T)^2 \tag{255}$$

$$= \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} \sigma_0 = \bar{u}\sigma_0 \tag{256}$$

This simple model recovers the hard-sphere collision frequency we began with.

The temperature dependence is predicted to be

$$k(T) = AT^{1/2}. \tag{257}$$

Very few reactions are well described by this model.

A better model might assign a higher probability of reaction to a head-on collision than to a glancing one. A simple application of this idea results in the "line of centers" model.

8.2 Line of centers model

For each value of u, there will be some critical value of b, called b_{max}. Collisions with that u and $b > b_{\text{max}}$ will not result in reaction; with $b \leq b_{\text{max}}$ reaction will occur.

To find b_{max} we require that the "energy along the line of centers", $\frac{1}{2}\mu v_{\text{loc}}^2$, be greater than some threshold value ε_0. Then we will have

$$\sigma(\varepsilon_t) = \sigma(\frac{1}{2}\mu u^2) = \pi b_{\text{max}}^2(u). \tag{258}$$

Figure 19:

From the diagram, we have

$$\frac{b}{d} = \cos\left(\frac{\pi}{2} - \varphi\right) = \sin\varphi \tag{259}$$

$$v_{\text{loc}} = u\cos\varphi = u(1 - \sin^2\varphi)^{1/2} \tag{260}$$

$$v_{\text{loc}} = u\left(1 - \left(\frac{b}{d}\right)^2\right)^{1/2} \tag{261}$$

We require

$$\frac{1}{2}\mu v_{\text{loc}}^2 \geq \varepsilon_0, \tag{262}$$

where the equality holds at $b = b_{\text{max}}$.

$$\underbrace{\frac{1}{2}\mu u^2}_{\varepsilon_t}\left(1 - \left(\frac{b}{d}\right)^2\right) \geq \varepsilon_0 \tag{263}$$

$$1 - \frac{b_{\text{max}}^2}{d^2} = \frac{\varepsilon_0}{\varepsilon_t} \tag{264}$$

$$b_{\max}^2 = d^2 \left(\frac{\varepsilon_t - \varepsilon_0}{\varepsilon_t} \right) \tag{265}$$

So

$$\sigma(\varepsilon_t) = \pi b_{\max}^2 = \pi d^2 \left(\frac{\varepsilon_t - \varepsilon_0}{\varepsilon_t} \right) \tag{266}$$

$$\tag{267}$$

when $\varepsilon_t \geq \varepsilon_0$, and $\sigma(\varepsilon_t) = 0$ otherwise.

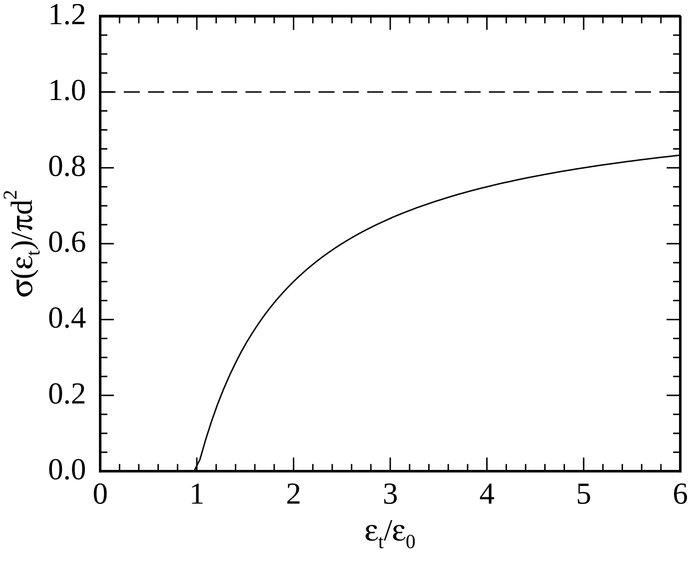

Figure 20: "Line of centers" cross section as a function of translational energy.

With this $\sigma(\varepsilon_t)$, we evaluate $k(T)$

$$k(T) = \frac{8\pi}{\mu^2} \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \sigma_0 \int_{\varepsilon_0}^{\infty} \left(\frac{\varepsilon_t - \varepsilon_0}{\varepsilon_t} \right) \varepsilon_t e^{-\varepsilon_t / k_B T} d\varepsilon_t \tag{268}$$

Integrate by parts to obtain

$$k(T) = \frac{8\pi}{\mu^2} \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \sigma_0 e^{-\varepsilon_0 / k_B T} (k_B T)^2 \tag{269}$$

$$k(T) = \underbrace{\left(\frac{8 k_B T}{\pi \mu} \right)^{1/2}}_{\text{volume “swept out” by one molecule each second}} \sigma_0 \underbrace{e^{-\varepsilon_0 / k_b T}}_{\text{fraction of collisions effective in producing reactions}} \tag{270}$$

This formula is the "SCT" or "LOC" rate coefficient definition.

Predicted temperature dependence is

$$k(T) = AT^{1/2}e^{-\varepsilon_0/k_BT} \tag{271}$$

What is the predicted activation energy?

$$E_a \equiv RT^2 \frac{d(\ln k)}{dT} \tag{272}$$

where we use R for molar units, k_B for molecular units. Then

$$\ln k = \ln A + \frac{1}{2}\ln T - \varepsilon_0/k_BT \tag{273}$$

$$\frac{d(\ln k)}{dT} = \frac{1}{2T} + \frac{\varepsilon_0}{k_BT^2} \tag{274}$$

$$E_a = \varepsilon_0 + \frac{1}{2}k_BT \tag{275}$$

So the activation energy E_a is equal to ε_0 at $T = 0$ (where the rate also equals 0!) and rises linearly with T after that.

In general, a $k(T)$ expression

$$k(T) = AT^m e^{-E_b/RT} \tag{276}$$

will have activation energy

$$E_a = E_b + mRT. \tag{277}$$

8.3 "Arrhenius" cross section

Here I want to apply a cross section

$$\sigma(\varepsilon_t) = C\frac{(\varepsilon_t - \varepsilon_0)^{1/2}}{\varepsilon_t} \tag{278}$$

for $\varepsilon_t > \varepsilon_0$, and $\sigma(\varepsilon_t) = 0$ otherwise. C has units of $(\text{energy})^{1/2} \cdot \text{m}^2$.

Inserting this into Eq. (248) for $k(T)$, we have

$$k(T) = (\text{constant})\int_0^\infty (\varepsilon_t - \varepsilon_0)^{1/2} e^{-\varepsilon_t/k_BT} d\varepsilon_t \tag{279}$$

Change variable to $y = (\varepsilon_t - \varepsilon_0)^{1/2}$, integrate by parts (twice), and use the Gaussian integral

$$\int_0^\infty e^{-a^2x^2}dx = \frac{\sqrt{\pi}}{2a}. \tag{280}$$

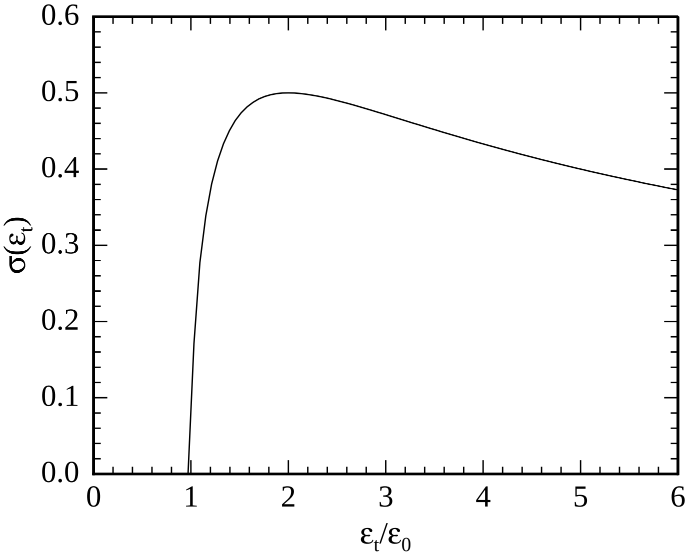

Figure 21: Special cross section

Collecting constants gives

$$k(T) = \frac{2C}{(2\mu)^{1/2}} e^{-\varepsilon_0/k_B T} \tag{281}$$

Finally, we have arrived at something that looks like the Arrhenius equation, with E_a independent of temperature.

In fact, this particular form for $\sigma(\varepsilon_t)$ is the *only* one which gives a T-independent E_a. Since the Arrhenius equation is so successful and widely used, one might be tempted to believe that

$$\sigma(\varepsilon_t) \propto \frac{(\varepsilon_t - \varepsilon_0)^{1/2}}{\varepsilon_t} \tag{282}$$

for most chemical reactions. No; most reactions are studied over a rather narrow T range (perhaps 0 to 100 ^{0}C, for example), and over that small a range deviations from Arrhenius behavior are hard to see.

Now that we have the idea of a collision-energy-dependent reaction cross section $\sigma(\varepsilon_t)$ in hand, I can give a physical interpretation of E_a. This interpretation is known as *Tolman's theorem*: E_a give the difference between the average energy of *reacting* molecules and the average energy of all molecules in the sample.

Note that only for the special shape $\sigma(\varepsilon_t) \propto \frac{(\varepsilon_t - \varepsilon_0)^{1/2}}{\varepsilon_t}$ do the two averages move together with changing T.

Figure 22:

8.4 Direct application of SCT

Let's compare some "LOC" results with experimental ones. For a collection of atom-transfer reactions whose kinetics have been measured, we can compare experimental A-factors (also called the frequency factor) to LOC ones if we take the experimental E_a as a reasonable estimate of ε_0. Other necessary data are hard-sphere radii σ_0, obtained from gas viscosity measurements. (That is, looked up.) Table 4 gives values from some homolytic hydrogen atom transfer reactions in the gas phase. The SCT rates are almost always too large, and they are much too large for more complicated reactants.

Table 4 Measured and calculated (by the line of centers model) A-factors for a few H-atom transfer reactions.

reaction	$\log_{10} A_{\text{exp}} / \text{M}^{-1}\,\text{s}^{-1}$	$\log_{10} A_{\text{LOC}}$
$\text{H} + \text{HCl} \longrightarrow \text{H}_2 + \text{Cl}$	10.36	11.77
$\text{H} + \text{HBr} \longrightarrow \text{H}_2 + \text{Br}$	11.04	12.16
$\text{H} + \text{HI} \longrightarrow \text{H}_2 + \text{I}$	10.70	12.13
$\text{CH}_3 + \text{H}_2 \longrightarrow \text{CH}_4 + \text{H}$	8.60	11.62
$\text{CH}_3 + n\text{C}_4\text{H}_{10} \longrightarrow \text{CH}_4 + \text{C}_4\text{H}_9$	8.08	11.56
$\text{CH}_3 + \text{C}_6\text{H}_6 \longrightarrow \text{CH}_4 + \text{C}_6\text{H}_5$	7.40	11.97

One interpretation is that the molecular orientations might make a difference. To account for that, we might introduce a "steric factor" p to fix up the agreement between theory and experiment:

$$p = \frac{A_{\text{exp}}}{A_{\text{SCT}}}. \tag{283}$$

Typical values of p must be $10^{-4} - 10^{-1}$; smaller values reflect tighter constraints on the geometry of an encounter. Now the "predicted" rate coefficient is

$$k_{\text{fixed}}(T) = p\bar{u}\sigma_0 e^{-\varepsilon_0/k_B T} \tag{284}$$

where the average relative speed $\bar{u}$ is $\left(\frac{8k_B T}{\pi\mu}\right)^{1/2}$ as before.

In the 20s and 30s, considerable effort was expended trying to find good ways to predict p. However, as it became clear that several factors other than simple steric ones were important, this approach was largely abandoned.

9 Thermodynamic connection

Can we find a connection between the measured activation energies (or postulated threshold energies) and real thermodynamic quantities? Maybe.

Consider a reversible, elementary reaction of ideal gases:

$$\mathrm{A} \underset{k_2(T)}{\overset{k_1(T)}{\rightleftharpoons}} \mathrm{B} \tag{285}$$

If k_1 and k_2 follow the Arrhenius equation over the experimental temperature range,

$$k_1 = A_1 e^{-E_1/RT} \tag{286}$$

$$k_2 = A_2 e^{-E_2/RT} \tag{287}$$

At any T, the equilibrium constant K° is

$$K^\circ = \frac{P_{\mathrm{B,eq}}/P^\circ}{P_{\mathrm{A,eq}}/P^\circ} = \frac{k_1(T)}{k_2(T)}, \tag{288}$$

where the standard state is the ideal gas with pressure $P^\circ = 1$ bar. In this case, since the reactants and products are ideal gases and the same number of moles of gas is present before and after the reaction, the rate coefficients may be written in any units and the last equality holds. For reactions that change the number of moles, or reactions in solution, the rate coefficients must be written in the units specified by the thermodynamic standard state.

Thermodynamics gives us

$$K^\circ(T) = \exp(-\Delta G^\circ/RT) \tag{289}$$

where

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{290}$$

In using Eq. (289), it is important to keep track of standard states, because K° is always dimensionless and extracting useful concentrations or pressures from it demands that you pay attention to the standard states. Any modern physical chemistry textbook should give a careful description; I like the treatment in Levine, *Physical Chemistry*, 4th ed. (McGraw-Hill, 1995).

In this reaction, for which the number of moles of gas does not change, and also approximately for solution reactions,

$$\Delta H^\circ = \Delta E^\circ + \Delta(PV) \tag{291}$$

$$\approx \Delta E^\circ \tag{292}$$

so that

$$K^\circ(T) = \exp\left(\frac{-\Delta E^\circ + T\Delta S^\circ}{RT}\right) \tag{293}$$

$$= e^{\Delta S^\circ/R} e^{-\Delta E^\circ/RT} \tag{294}$$

Then

$$\frac{k_1(T)}{k_2(T)} = \frac{A_1}{A_2} e^{-(E_1-E_2)/RT} = e^{\Delta S^\circ/R} e^{-\Delta E^\circ/RT}, \tag{295}$$

and it seems reasonable to identify $\frac{A_1}{A_2}$ with $e^{\Delta S^\circ/R}$, and $E_1 - E_2$ with ΔE°. (This is a plausible interpretation, not a proof!) Figure 23 shows the interpretation.

Figure 23: Thermodynamic interpretation of the difference in forward and reverse activation energies.

ΔE° is a perfectly well-defined thermodynamic quantity; A and B are stable substances with measurable equilibrium properties. $()^\ddagger$ may or may not possess thermodynamic properties; if all reactions go through a well-defined transition state, it is reasonable to ascribe an E° to that state. E_1 and E_2 are empirical kinetic parameters.

If we can get away with this bit of weak thermodynamics, it has useful applications. For instance, thermodynamic properties of unstable intermediates can be estimated. Consider

$$\mathrm{Br} + \mathrm{CH_4} \underset{\mathrm{k_2}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{HBr} + \mathrm{CH_3} \tag{296}$$

If the activation energies in the forward and reverse directions can be measured, then the overall ΔE° for the reaction is given by their difference. Since ΔE° of formation for all species except CH_3 is already known, we can then calculate ΔE° for formation of CH_3.

Possible problems with this “calorimetry through kinetics”:

1. Kinetic data are generally less accurate than thermodynamic data.

2. Our interpretation has depended on $\mathrm{A} \rightleftharpoons \mathrm{B}$ being an elementary reaction. It's easy to confuse an E_a measured for unresolved composite reactions with an elementary E_a. Then, $k_1/k_2 \neq K^\circ$.

3. $()^\ddagger$ might not be sufficiently well-defined to have a real E°; different molecular encounters might travel along quite different paths. This behavior can appear as strongly T-dependent Arrhenius parameters in some cases.

In practice, the third problem is often swamped by the first.

The idea that $()^\ddagger$ might have useful thermodynamic properties is expanded in *transition state theory*, which we will begin studying next week.

9.1 Activation energies and catalysis

.

Consider a reaction with uncatalyzed and catalyzed pathways:

$$\mathrm{A} \xrightarrow{\mathrm{k_u}} \mathrm{P} \tag{297}$$

$$\mathrm{A} + \mathrm{C} \xrightarrow{\mathrm{k_c}} \mathrm{P} + \mathrm{C} \tag{298}$$

The catalyst is providing a new pathway with a new transition state, as illustrated in the left panel of Figure 24.

Figure 24: Correct (left panel) and incorrect (right panel) interpretations of the effect of a catalyst.

Often the statement is made that the catalyst lowers the activation energy for the reaction. That's right, but subject to some misinterpretation.

Why can't, for example, the catalyst raise the E° of the reactants, lowering E_1 and leaving E_2 the same, as in the right panel of Figure 24?

Here's a moneymaking scheme that works if this second possibility is available. Allow a mixture of A and P to come to equilibrium. Then add the catalyst. Since $E^\circ(\mathrm{A})$ increases, the equilibrium constant shifts; the reaction will move toward products, releasing heat. Use that heat to do some work, or sell it. Then remove the catalyst (which is unchanged by definition.) The reaction will shift back to the left, absorbing heat from the surroundings. This violates the Second Law of Thermodynamics. Equilibria are unaffected by catalysts; only rates are affected.

10 Predicting rate coefficients

The basic problem: there is no easy, cheap, accurate way. I think of the approaches that are commonly used in three groups:

Empirical methods These attempt to predict rate coefficients for particular reactions by relating them to rates of similar reactions that have already been measured.

Statistical rate theories These make assumptions about the time scales of intramolecular energy flow and reaction. The most important are *transition state theory* (TST) and its extensions, and the closely related theory called RRKM for unimolecular and recombination reactions.

Dynamical theories These attempt to predict rates by explicitly following the motions of atoms in time. They are capable of essentially perfect accuracy in principle, but are impossible to carry out except for the simplest three- and four-atom reactions.

I will give an overview of several successful empirical methods, with references but not much detail.

10.1 Empirical Methods

10.1.1 Evans-Polanyi-Semenov correlation

E_a vs. ΔE:

$$E_a = \alpha \Delta E + C, \tag{299}$$

where α and C are empirical fitting constants and ΔE is the thermodynamic ΔE (or ΔH) for the reaction.

For example, for a series of atom-transfer reactions

$$\mathrm{X}\cdot + \mathrm{RH} \rightarrow \mathrm{Hx} + \mathrm{R}\cdot \tag{300}$$

Variation of R, but maintaining the same fitting parameters for all Rs with primary H, (for example) might work.

Similarly, it is sometimes useful to correlate bond dissociation energies against activation energies. These correlations work decently, especially for atom transfer reactions, but the reactions in a correlated series must be fairly closely related. Figure 25 shows an example. Moore and Pearson is a good reference.

10.1.2 Bond energy - bond order method (BEBO)

This “semiempirical” method is described in H.S. Johnston, *Gas Phase Reaction Rate Theory*. This theory attempts to predict activation energies without using measured rates for similar reactions. Instead, it uses empirical correlations with other (spectroscopic and thermochemical) data. It works well for H-atom transfer and somewhat less well for other atom transfers. It has largely been superseded by modern TST.

Figure 25: Evans-Polyani-Semenov plot, from Moore and Pearson:

10.1.3 Benson's rules

The primary reference is S. Benson, *Thermochemical Kinetics*. Benson gives a list of suggestions for estimating values needed in the "thermodynamic TST" expression

$$k(\mathrm{T}) = \frac{k_B T}{h} \exp\left[\frac{\Delta S_0^{\ddagger}}{R}\right] \exp\left[\frac{-\Delta H_0^{\ddagger}}{RT}\right] (c^{\ominus})^{\Delta n^{\ddagger}} \tag{301}$$

(We'll derive this expression later). Benson's rules allow estimation of $\Delta S_0^{\ddagger}$ and $\Delta H_0^{\ddagger}$ on the basis of characteristics of different types of reactions, for both gas-phase and solution. He gives tables of "group contributions": for example, $\Delta \mathrm{S}_0^{\ddagger}$ for a hydrocarbon reaction will be increased by so much if a methyl group is added to a molecule.

These rules and similar ones are widely used, especially in chemical engineering. For fast estimates of organic reaction rates, Benson's rules are often the method of choice.

10.1.4 Linear free energy correlations

Espenson describes several, the most famous being the Hammett equation that correlates rates for reactions of m- and p- substituted aromatics with different substituents. These are widely successful in physical organic chemistry. I defer discussion until we cover reactions in solution explicitly.

10.1.5 Computational Approaches

Several modern quantum chemistry programs (Gaussian, GAMESS, etc.) will attempt to calculate energies and other properties of transition states (and therefore activation energies) for medium-sized molecules. These techniques are getting better all the time. It is absolutely necessary to do a calculation which includes some form of electron correlation (MCSCF, CI, CCSD, etc.) in order to obtain reactive properties correctly. Density functional theory is rapidly gaining popularity for this purpose.

10.2 Introduction to Potential Energy (hyper) Surfaces

A collection of N atoms requires $3N$ coordinates to specify positions of all nuclei. 3 coordinates specify the location of the center of mass (COM). 3 coordinates specify orientation in space (only 2 are required for linear molecules.) So $3N - 6$ relative coordinates describe "internal" positions.

Use the Born-Oppenheimer approximation to separate motions of nuclei and electrons; then write an effective potential for the nuclei as function of nuclear positions. The effective potential as a function of nuclear position is the "potential energy hypersurface", usually called "potential surface", PES, or simply "potential".

"Effective potential" means total internal energy of the molecular system *except* nuclear kinetic energy.

10.2.1 Diatomic Molecules

$3N - 5 = 1$ we only need a one-dimensional potential surface: a potential energy curve. The only possible reaction here is dissociation; the natural "reaction coordinate" is the internuclear distance.

10.2.2 Linear Triatomic System

For a triatomic, $N = 3$, so $3N - 5 = 4$, and we should properly have a potential surface that depends on 4 coordinates. To simplify the problem let us consider only collinear arrangements; this restricts 2 internal bending coordinates, and we are left with 2 independent coordinates. The potential energy surface is usually drawn as a contour map, as in Figure 26.

Figure 26: Generic 2D potential surface for a linear triatomic problem.

If we plot V as function of distance along minimum energy path, we get something like a traditional reaction coordinate diagram, as in Figure 27. It's sometimes convenient to make a new coordinate system which has one axis parallel to the minimum energy path at the saddle point, as in the top panel of Figure 27. Then plots of V vs the new coordinates show a distinct maximum in the reaction coordinate and a minumum in the other direction. The properties of the surface at the saddle point play an important role in predictions of rates.

For more complicated reactions than linear triatomic atom transfers, the

Figure 27:

potential surface is hard to draw. But there is usually still one coordinate, the "reaction coordinate", along which the potential has a maximum at the saddle point. All other coordinates show *minima* in the potential at the saddle point. The quantum chemistry programs search for transition states by looking for these points with maxima along single axes and minima along all others.

10.2.3 Trajectories

One way to model kinetics is to "shoot marbles along the potential surface". To do this it is very useful to introduce new coordinates that are appropriate for AB + C systems of different masses.

Figure 28:

$$r_1 = x - y \tan\theta \tag{302}$$

$$r_2 = \alpha y \sec\theta \tag{303}$$

where

$$\sin\Theta = \left[\frac{M_A M_C}{(M_A + M_B)(M_B + M_C)}\right]^{1/2} \tag{304}$$

$$\alpha = \left[\frac{M_A(M_B + M_C)}{M_C(MA + M_B)}\right]^{1/2} \tag{305}$$

These "skewed and scaled coordinates" can be used in classical trajectory calculations to predict vibrational and translational effects in reactions.

10.3 Transition State Theory

This material is covered minimally in Espenson section 7–7, and better in Chap. 10 of SFH; these notes follow the SFH treatment. Good descriptions may also be found in Laidler (section 4.5) and Moore & Pearson.

TST is a procedure for calculating A-factors for reactions. It is also known as “activated complex theory”, and sometimes by the older and more optimistic name “absolute rate theory”.

It makes the following assumptions:

1. The Born-Oppenheimer approximation applies to reacting molecules.
2. There is a Boltzmann distribution of reactant molecule internal states.
3. There is a “dividing surface” at the saddle point; once a reacting pair of molecules has crossed it, it cannot turn back. Some authors (including SFH) regard this as the “fundamental assumption” of TST.
4. At the saddle point, motion along the reaction coordinate is “free”; it is not coupled with other motions.
5. In the transition state, the Boltzmann distribution continues to describe the reacting molecules’ internal states.

Figure 29: Potential energy along the minimum energy path.

10.4 Derivation

Consider the elementary reactions

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X}^{\ddagger} \rightarrow \mathrm{C}, \tag{306}$$

whose reaction coordinate diagram is shown in Figure 29. δ is an arbitrary (but small) "thickness" of the transition-state region along the reaction coordinate.

We know that at complete equilibrium,

$$[\mathrm{X}^\ddagger] = N^\ddagger = K_c^\ddagger[\mathrm{A}][\mathrm{B}] \tag{307}$$

and that if we break all the $\mathrm{X}^\ddagger$ into two groups, one going forward ($N_f^\ddagger$) and one backward ($N_b^\ddagger$), those two must be equal:

$$N_f^\ddagger = N_b^\ddagger = \frac{1}{2}N^\ddagger \tag{308}$$

Now if all the product molecules (and therefore $N_b^\ddagger$) were all taken away, the concentration $N_f^\ddagger$ would be for the moment unchanged. So,

$$N_f^\ddagger = \frac{1}{2}N^\ddagger = \frac{1}{2}K_c^\ddagger[\mathrm{A}][\mathrm{B}] \tag{309}$$

This situation is called "quasiequilibrium."

Those forward-moving transition states have an average velocity $\bar{v}_s$. They will require an average time $\frac{\delta}{\bar{v}_s}$ to cross the transition region, so the concentration of product molecules formed per second is

$$N_f^\ddagger \frac{\bar{v}_s}{\delta} = \frac{N^\ddagger}{2}\frac{\bar{v}_s}{\delta} \tag{310}$$

$$= \frac{K_c^\ddagger}{2}\frac{\bar{v}_s}{\delta}[\mathrm{A}][\mathrm{B}] \tag{311}$$

and we identify the rate coefficient

$$k = \frac{K_c^\ddagger}{2}\frac{\bar{v}_s}{\delta}. \tag{312}$$

We need to evaluate $K_c^\ddagger$ and $\bar{v}_s$.

To calculate $\bar{v}_s$, we use the one-dimensional Maxwell distribution of speeds. Note that the integration goes only from 0 to ∞ rather than from $-\infty$ to ∞, since we are interested only in those transition states that are moving along the reaction towards products and not those moving back toward reactants.

$$\bar{v}_s = \frac{\int_0^\infty v_s e^{-\frac{\mu_s v_s^2}{2k_BT}}\,dv_s}{\int_0^\infty e^{-\frac{\mu_s v_s^2}{2k_BT}}\,dv_s} = \left(\frac{2k_BT}{\pi\mu_s}\right)^{1/2} \tag{313}$$

To calculate $K_c^\ddagger$, we need statistical mechanics. The basic statistical mechanics expression for an equilibrium constant is

$$K_c^\ddagger = \frac{Q_{\mathrm{tot}}^\ddagger}{Q_A Q_B}e^{-E_0/k_BT}, \tag{314}$$

where the Q are partition functions, per unit volume, and E_0 is the difference between the zero point energies of the reactants and the transition state (the "classical barrier".)

We have assumed separability for the motion along the reaction coordinate; that means

$$Q^{\ddagger}_{\text{tot}} = Q^{\ddagger}_{S} Q^{\ddagger} \tag{315}$$

where $Q^{\ddagger}_{S}$ is the (1-dimensional) partition function for motion along the reaction coordinate, and $Q^{\ddagger}$ the partition function for all other motions of the transition state. Treating the motion along the reaction coordinate as translation in a box of length δ, we have

$$Q^{\ddagger}_{S} = (2\pi\mu_s k_B T)^{1/2} \frac{\delta}{h} \tag{316}$$

from elementary stat mech; $Q^{\ddagger}_{S}$ is dimensionless. So,

$$K^{\ddagger}_{c} = (2\pi\mu_s k_B T)^{1/2} \frac{\delta}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E_0/k_B T} \tag{317}$$

and substituting into the formula for k (with our expression for $\bar{v}_s$)

$$\begin{aligned} k &= \frac{k^{\ddagger}_{c}}{2} \frac{\bar{V}_s}{\delta} && (318) \\ &= (2\pi\mu_s k_B T)^{1/2} \frac{\delta}{2h} \left(\frac{2k_B T}{\pi\mu_s} \right)^{1/2} \frac{1}{\delta} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E_0/k_B T} && (319) \\ k &= \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E_0/k_B T} && (320) \end{aligned}$$

Eq. (320) is the basic transition state theory equation. Note that this expression is independent of δ and μ_s, which were artificial.

To calculate the rate, we need to know E_0 and be able to evaluate the partition functions. We can estimate E_0 from experimental activation energies, or try to measure it with more sophisticated experimental techniques, or try to calculate it with electronic structure theory. This last possibility is becoming more and more accessible and popular.

10.5 Partition Functions

For a single molecule,

$$Q \equiv \sum_i e^{-E_i/k_B T} \tag{321}$$

where the sum is over all *states* i, or

$$Q = \sum_j g_j \, e^{-E_j/k_B T} \tag{322}$$

where the sum is over all *energy levels* j and each level has degeneracy g_j. If we separate the energy into electronic, vibrational, rotation, and translational contributions,

$$E_j = e_j + v_j + r_j + t_j, \tag{323}$$

and similarly separate the degeneracies

$$g_j = g_c g_v g_r g_t, \tag{324}$$

then we can factor the partition function

$$Q = Q_{\text{el}} Q_v Q_r Q_t \tag{325}$$

and evaluate each degree of freedom separately.

The electronic partition function is

$$Q_{\text{el}} = \sum_i g_i e^{-e_i/k_B T}, \tag{326}$$

where i labels all the electronic states. Usually, the separation between the ground state ($e_i = 0$) and the higher states is much greater than $k_B T$, so that $Q_{\text{el}} \approx g_0$, the degeneracy of the ground state. Notable exceptions are $^2\Pi$ diatomics, such as NO and OH, which have two low-lying electronic energy levels that both have significant population at ordinary temperatures. Open-shell atoms behave similarly.

For the other degrees of freedom, the sums can be evaluated ahead of time to obtain closed-form expressions. The expressions and typical values are given in Table 5, taken from chapter 4 of Laidler.

To use these formulas, we need spectroscopic data on the reactants (usually not difficult to find) and the transition state (usually not available.) So, for the transition state, we can either guess the values on the basis of known values for similar molecules, or calculate them with electronic structure programs.

Rotational partition functions contain σ, the symmetry number. Laidler and SFH (and I) recommend that you ignore the σ in the rotational P.F.s and instead use a statistical factor $L^\ddagger$. $L^\ddagger$ is the number of different possible transition states (or sets of products) which you could form if all the identical atoms were labeled so you could tell them apart. For example, in the reaction

$$\text{H} + \text{CH}_4 \longrightarrow \text{H}_2 + \text{CH}_3 \tag{327}$$

Table 5 Partition function table from Laidler.

the statistical factor $L^{\ddagger}$ is 4:

$$\mathrm{H}^5 + \mathrm{CH}^1\mathrm{H}^2\mathrm{H}^3\mathrm{H}^4 \longrightarrow \mathrm{H}^5\mathrm{H}^1 + \mathrm{CH}^2\mathrm{H}^3\mathrm{H}^4, \tag{328}$$

etc.

For rotational partition functions you need moments of inertia, while spectroscopic tables generally give you rotational constants.

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 cI} \tag{329}$$

where $\tilde{B}$ is in cm^{-1} units, or

$$B = \frac{\hbar^2}{2I} \tag{330}$$

$$\tag{331}$$

with B in joule units.

Nonlinear molecules have three moments of inertia, called I_A, I_B, and I_C. In *symmetric tops*, two of the moments are the same. These come in two flavors: if the unique moment of inertia is smaller than the other two, the top is called prolate, while if the unique moment is larger than the other two, it is called oblate. Prolate is cigar-like, oblate is frisbee-like. For symmetric tops, then, only two rotational constants (not three) appear in spectroscopic tables, and you have to understand which one to use twice. The relations between the rotational constants and the moments of inertia are similar to that for diatomics:

$$\tilde{A} = \frac{h}{8\pi^2 c I_A} \tag{332}$$

$$\tilde{B} = \frac{h}{8\pi^2 c I_B} \tag{333}$$

For asymmetric tops the three rotational constants are all different.

The "working" TST expression is now (for ideal gases)

$$k = \frac{k_B T}{h} L^{\ddagger} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E_0/k_B T} \tag{334}$$

where $L^{\ddagger}$ is the "statistical factor" (SFH sec. 10.6.2), and $Q^{\ddagger}$ is the molecular partition function per unit volume for the transition state, *excluding* the motion along the reaction coordinate, and excluding any symmetry numbers. Q_A and Q_B are the molecular partition functions per unit volume for the reactants, excluding symmetry numbers.

This expression in terms of partition functions is strictly valid only for ideal gases. The expression for the equilibrium constant in terms of partition functions, Eq. (314), is true only in that case. For other systems, more sophisticated expressions for the equilibrium constant are needed; instead, TST is usually used in an alternative (but less predictive) "thermodynamic" form.

I now proceed to several examples of the use of TST with increasing complexity.

10.6 Collisions of hard spheres

10.6.1 Straightforward calculation

Consider the simplest case, a bimolecular reaction between hard spheres.

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products} \tag{335}$$

$$k(T) = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E_0^{\ddagger}/k_B T} \tag{336}$$

We need to use partition functions appropriate to the hard-sphere model. Hard spheres have no internal structure, so we have translational parts only for the reactants.

$$Q_A = \frac{(2\pi m_A k_B T)^{3/2}}{h^3} \tag{337}$$

$$Q_B = \frac{(2\pi m_B k_B T)^{3/2}}{h^3}, \tag{338}$$

where both have units m^{-3}. The transition state looks like two hard spheres touching, as shown in Figure 30, so its partition function is like that of a diatomic molecule. The reaction coordinate corresponds to the single vibrational mode of the diatomic, so we need not include that in $Q^{\ddagger}$; only the translational and rotational parts need to be included:

$$Q^{\ddagger} = Q_t^{\ddagger} Q_r^{\ddagger} \tag{339}$$

Figure 30:

$$Q_t^\ddagger = \frac{(2\pi(m_A + m_B)k_BT)^{3/2}}{h^3} \tag{340}$$

$$Q_r^\ddagger = \frac{8\pi^2 Ik_BT}{\sigma h^2}, \tag{341}$$

but we ignore σ (in this case it's 1 anyway).

To calculate $Q_r^\ddagger$ we need to calculate the moment of inertia. We find the center of mass with the two equations

$$x_A + x_B = r_A + r_B = d_{AB} \tag{342}$$

$$x_Am_A = x_Bm_B \tag{343}$$

The moment of inertia is $I = m_Ax_A^2 + m_Bx_B^2$. (Exercise: Show that $I = \mu d_{AB}^2$, where $\mu = \frac{m_Am_B}{m_A+m_B}$.) Then

$$Q_r^\ddagger = \frac{8\pi^2\mu d_{AB}^2k_BT}{h^2} \tag{344}$$

Now

$$k(T) = \frac{k_BT}{h}\frac{\frac{(2\pi(m_A+m_B)k_BT)^{3/2}}{h^3}\frac{8\pi^2\mu d_{AB}^2k_BT}{h^2}}{\frac{(2\pi(m_Ak_BT)^{3/2}}{h^3}\frac{(2\pi m_Bk_BT)^{3/2}}{h^3}}e^{-E_0^\ddagger/k_BT} \tag{345}$$

Lots of stuff cancels; we are left with

$$k(T) = (k_B T)^{1/2} \mu^{-1/2} \sqrt{8} \pi^{1/2} e^{-E_0^\ddagger / k_B T} d_{AB}^2 \tag{346}$$

$$= \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \pi d_{AB}^2 e^{-E_0^\ddagger / k_B T} \tag{347}$$

This is exactly the same formula we got from the line of centers model in simple collision theory! Note the origin of the πd_{AB}^2 term (the cross section) in the TST rate. It came from the rotational partition function. Greater d_{AB} and greater masses make for larger densities of rotational states, and therefore greater statistical factors in the rate. $E_0^\ddagger$, as before, is the difference in ground-state energies of the reactants and transition state.

What is E_a?

$$E_a = k_B T^2 \frac{d(\ln k)}{dT} \tag{348}$$

$$= k_B T^2 \frac{d}{dT} \left(\frac{1}{2} \ln T - \frac{E_0^\ddagger}{k_B T} + \text{constant} \right) \tag{349}$$

$$= k_B T^2 \left(\frac{1}{2T} + \frac{E_0^\ddagger}{k_B T^2} \right) \tag{350}$$

$$= \frac{1}{2} k_B T + E_0^\ddagger, \tag{351}$$

as expected.

Let's look at a couple of quick-and-dirty estimates we can make from the TST rate expression without actually doing any calculations.

10.6.2 Temperature dependence

Looking at Table 5 we see that both translational and rotational partition functions contribute a factor of $T^{1/2}$ per degree of freedom so we expect to have

$$k(T) \sim \frac{k_B T}{h} \frac{\overset{Q_t^\ddagger}{(T^{3/2})}\overset{Q_r^\ddagger}{(T)}}{\underset{Q_A}{(T^{3/2})}\underset{Q_B}{(\mathrm{T}^{3/2})}} e^{-E_0^\ddagger / k_B T} \tag{352}$$

so the overall T dependence looks like

$$k(T) \sim T^{1/2} e^{-E_0^\ddagger / k_B T} \tag{353}$$

We could have immediately written down the expected formula for E_a from this estimate.

10.6.3 Order of magnitude of preexponential factor

Using the rough numbers from Table 5 we have

$$k(T) = \frac{k_B T}{h} \frac{q_t^3 q_r^2}{q_t^3 q_t^3} e^{-E_0/k_B T} \tag{354}$$

where q_t and q_r indicate per degree of freedom. So wehave

$$A \sim \frac{(10^{31})(10^2)}{(10^{31})(10^{31})} \frac{k_B T}{h} \tag{355}$$

$\frac{k_B T}{h}$ has the value $6.25 \times 10^{12}\ \mathrm{s}^{-1}$ at 300 K, so

$$A \sim (10^{-29}\ \mathrm{m}^3)(6 \times 10^{12}\ \mathrm{s}^{-1}) \tag{356}$$

$$\sim 6 \times 10^{-17}\ \mathrm{s}^{-1}\ \mathrm{m}^3 \tag{357}$$

$$\sim 6 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1} \tag{358}$$

where these units include an implied "per molecule". This is a typical A for a fast gas phase bimolecular reaction. For a reasonable set of μ, πd_{AB}^2, Eq. (347) gives $A = 2.4 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{molec}^{-1}\ \mathrm{s}^{-1}$. So our order-of-magnitude estimate is not too bad.

To give you a feeling for magnitudes of bimolecular rate coefficients,

$$10^{-11} \frac{\mathrm{cm}^3}{\mathrm{molec} \cdot \mathrm{s}} \mathrel{\hat{=}} 6 \times 10^{12} \frac{\mathrm{cm}^3}{\mathrm{mol} \cdot \mathrm{s}} \mathrel{\hat{=}} 6 \times 10^{9} \frac{\mathrm{L}}{\mathrm{mol} \cdot \mathrm{s}} \tag{359}$$

Since $K_c^\ddagger$ is a concentration equilibrium constant,

$$\frac{d(\ln K_c^\ddagger)}{dT} = \frac{\Delta E_0^\ddagger}{RT^2} \tag{360}$$

$$\frac{d(\ln k)}{dT} = \frac{d}{dT}\left(\ln\left[\frac{k_B T}{h} K_c^\ddagger\right]\right) \tag{361}$$

$$= \frac{1}{T} + \frac{\Delta E_0^\ddagger}{RT^2} \tag{362}$$

$$E_a = RT^2 \frac{d(\ln k)}{dT} = \Delta E_0^\ddagger + RT \tag{363}$$

At constant pressure,

$$\Delta H_0^\ddagger = \Delta E_0^\ddagger + P(\Delta V_0^\ddagger), \tag{364}$$

where $\Delta V_0^\ddagger$ is called the "standard volume of activation". For unimolecular gas-phase or solution reactions, $\Delta V_0^\ddagger \approx 0$. Then

$$\Delta H_0^\ddagger = \Delta E_0^\ddagger \tag{365}$$

and so

$$E_a = \Delta H_0^\ddagger + RT \tag{366}$$

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S_0^\ddagger}{R}\right) \exp\left(-\frac{E_a}{RT}\right) \exp\left(\frac{RT}{RT}\right) (c^\ominus)^{\Delta n^\ddagger} \tag{367}$$

$$k = e\frac{k_B T}{h} \exp\left(\frac{\Delta S_0^\ddagger}{R}\right) \exp\left(-\frac{E_a}{RT}\right) (c^\ominus)^{\Delta n^\ddagger} \tag{368}$$

So, from the Arrhenius parameters we can obtain $\Delta S_0^\ddagger, \Delta H_0^\ddagger, \Delta E_0^\ddagger$;

$$A = e\frac{k_B T}{h} \exp\left(\frac{\Delta S_0^\ddagger}{R}\right) (c^\ominus)^{\Delta n^\ddagger} \tag{369}$$

for solution or unimolecular reactions. For bimolecular reactions, assuming ideal gas behavior,

$$P(\Delta V_0^\ddagger) = \Delta n^\ddagger RT \tag{370}$$

so

$$E_a = \Delta H_0^\ddagger + RT(1 - \Delta n^\ddagger) \tag{371}$$

and

$$k = e^{(1-\Delta n^\ddagger)} \frac{k_B T}{h} \exp\left(\frac{\Delta S_0^\ddagger}{R}\right) \exp\left(\frac{E_a}{RT}\right) (c^\ominus)^{\Delta n^\ddagger} \tag{372}$$

Thermodynamic TST is not really a predictive theory, though it is possible to empirically estimate enthalpies and entropies of activation, for instance, through Benson's rules. But it is very widely used as a descriptive framework for the interpretation of kinetic data. Volumes, entropies, and enthalpies of activation may be related to changes in molecular structure when the transition state is formed. Espenson's chapter 7 gives several examples of this sort of interpretative use of TST. (Section 7.4 should be ignored; such correlations are nearly always spurious and chemical interpretations are extremely dangerous. See McBane, *J. Chem. Educ.* **75**, 919 (1998).)

As the paper by Robinson points out, it is important to keep track of the standard states used for the activation parameters. It's very easy to find entropies of activation in the literature whose numerical values are meaningless because of errors in units of the rate coefficient.

11 Extensions to TST

Two important classes of modifications to classical TST are typically used today.

1. Quantum corrections, especially for tunneling. These account for the possibility that light atoms such as H and D might tunnel through the saddle-point barrier rather than climbing over it.

2. Variational TST, which attempts to minimize the effects of recrossing. Since recrossing always makes TST predict too large a rate, variational TST simply tries different configurations as the transition state (most of which are not "at the top of the barrier") until it finds the one that gives the lowest rate.

11.1 Tunneling corrections

There are several different kinds of tunneling corrections, but all are based on the quantum mechanical idea of a partical tunneling through a barrier. When a particle with kinetic energy E_t approaches a barrier of height E_0, in classical mechanics the particle will pass over if $E_t > E_0$ and be reflected back if $E_t < E_0$. (If $E_t = E_0$, it will spend forever trying to reach the top.) But in quantum mechanics, all energies have nonzero probabilities of both transmission and reflection.

Figure 31: Classical and quantum particles approaching barriers.

11.1.1 Tunneling correction

The one-dimensional Wigner correction is the simplest tunneling correction. It assumes that the reaction barrier may be approximated by an inverted parabola near the transition state:

$$V(s) = V_0 - \frac{1}{2} m \omega^{\ddagger} s^2, \tag{373}$$

where V_0 gives the potential at the top of the barrier, and $\omega^{\ddagger}$ is the magnitude of the "imaginary frequency" at the barrier. (If the barrier were inverted to form a potential well, the well would be a harmonic oscillator with angular frequency $\omega^{\ddagger} = (k/m)^{1/2}$; k is the force constant and m is the reduced mass for the harmonic motion.) Then at low temperatures ($k_B T \ll V_0$), the tunneling correction factor κ is

$$\kappa(T) = 1 + \frac{1}{24} \left(\frac{\hbar \omega^{\ddagger}}{k_B T} \right) \tag{374}$$

More sophisticated tunneling methods either assume a more realistic shape for the potential barrier, or try to account for the possibility that the tunneling might occur through a different part of the barrier than right at the transition state.

Tunneling is important when

1. the temperature is low ($k_B T \ll V_0$),
2. the atoms moving at the transition state are light (that is, are H or D), and
3. the barrier at the transition state is narrow (thin).

Tunneling corrections always make the rate larger than that predicted by classical TST.

11.1.2 Variational TST

We have been putting the dividing surface at the maximum in potential energy along the reaction path. It might be that that is not the best place.

Consider a reaction path that has a broad, open climb to the "summit" (saddle point) but shortly thereafter has a very narrow channel or passageway to products:

Figure 32:

Many trajectories might make it over the saddle point, but not find the "door" into the product region and get bounced back toward reactants. These recrossing trajectories get counted as product in normal TST, and contribute to a too-large estimate of the rate coefficient.

If we have a reliable way to predict transition state *properties* (vibrational frequencies, rotational constants) as a function of transition state *structure* (nuclear positions), then there is a way to solve this problem. Recrossing will always produce a TST rate which is too high. If we calculate the TST rate as a function of transition state structure, and choose the structure which gives the minimum rate, the TS will find its way to the "doorway" and recrossing will be minimized.

This procedure, called variational TST, is equivalent to placing the dividing surface at the point of maximum Gibbs function (rather than potential energy) along the reaction path.

Two programs are freely available to do these variational TST calculations. The grandaddy program is POLYRATE, from D. Truhlar's group at University of Minnesota. It is available at `http://comp.chem.umn.edu/WWW/POLYRATE/POLYRATE.html`. It has many, many options, and versions that attempt to account for solvent effects as well.

The other is TheRate (THEoretical RATEs), at `http://therate.hec.cetah.edu`. It has many fewer options; it uses only Gaussian for electronic structure data. You give the program Gaussian output files for the reactants, TS, and products. It gives you a list of predicted rates at temperatures of your choice, with or without tunneling corrections.

If you want to do variational TST, it produces a set of Gaussian input files at locations it needs; you run those, and it then reads their output.

11.2 Microcanonical TST

"Microcanonical" means "at fixed energy" rather than "at fixed temperature". The goal is to calculate a rate coefficient for a collection of molecules all with the same energy E.

To go from the microcanonical rate coefficient $k(E)$ to the canonical one $k(T)$, you average over an energy distribution:

$$k(T) = \int_0^\infty P(E)k(E)dE. \tag{375}$$

SFH derives the microcanonical rate constant (section 10.7), using classical statistical mechanics. The result is

$$k(E) = \frac{G^\ddagger(E - E_0)}{hN(E)} \tag{376}$$

where $G^\ddagger()$ is the *sum of states* of the transition state of energy $E - E_0$. This is the total number of transition-state quantum states at energy E (dimensionless).

$N(E)$ is the density of states of the reactants at energy E. Units are $(\text{energy})^{-1}$ (typically states-per-wavenumber.) $N(E) = \frac{dG(E)}{dE}$.

This formula is important in the version of TST best suited to unimolecular reactions, called RRKM theory.

Figure 33:

11.2.1 Sum and Density of States

The allowed energy levels for molecules generally become more numerous as the energy increases:

The density of states $N(E)$ is the number in a small interval δE. The number of states $G(E)$ is the total number below energy E.

11.3 Unimolecular Reactions - further development and overview

Basic mechanism

$$\mathrm{A + M} \quad \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \quad \mathrm{A^* + M} \tag{377}$$

$$\mathrm{A^*} \quad \xrightarrow{\mathrm{k}_2} \quad \mathrm{P} \tag{378}$$

SSA on A* gives

$$\text{rate} = k_{\text{uni}}[\mathrm{A}] = \frac{k_1 k_2 [\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} \tag{379}$$

Notation: E_0 is minimum energy required for the step A* → P to occur.

E is the energy actually contained in an A* molecule.

Increasingly sophisticated theories try to do more realistic jobs of estimating k_1, k_{-1}, and k_2.

1) Lindemann: Calculate k_1 from LOC/SCT, threshold E_0.
Assume k_{-1} is the collision rate $\bar{v}\sigma$
Assume k_2 is independent of E.

2) Hinshelwood: Retain assumptions that k_2 is independent of E and that $k_{-1} = \hat{v}\sigma$.

Estimate k_1 by using classical stat mech to evaluate the "equilibrium constant" k_1/k_{-1}, assuming that a molecule contains $\leqq$ classical oscillators.

Then

$$k_1 = \frac{\hat{v}\sigma}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} e^{-E_0/k_B T} \tag{380}$$

These k_1s can be much larger than SCT; for $E_0/k_B T = 10$ and $s = 5$, k_1 increases by a factor of 500 over SCT.

Remaining problem: s is empirically not equal to the number of vibrational modes, and it isn't clear why. Also the T dependence is very poorly predicted.

3) Classical RRK (Rice-Ramsperger-Kassel)

Allow for k_2 to change with E.

$$\mathrm{k}_2 \rightarrow \mathrm{k}_2(\mathrm{E}) \equiv \mathrm{k}(\mathrm{E}) \tag{381}$$

We continue to assume that $k_{-1} = \hat{v}\sigma$, but we must modify the notation to allow for different rates of production of A* with different E.

$$\mathrm{A + M} \quad \underset{\mathrm{k}_{-1}}{\overset{\mathrm{dk}_1(\mathrm{E})}{\rightleftharpoons}} \quad \mathrm{A^*(E, E + dE) + M} \tag{382}$$

$$\mathrm{A^*(E, E + dE)} \quad \xrightarrow{\mathrm{k(E)}} \quad \mathrm{P} \tag{383}$$

Define a corresponding differential unimolecular rate constant, the contribution a particular E makes to k_{uni}:

$$dk_{\text{uni}}(E, E+dE) = \frac{k(\mathrm{E})\frac{\mathrm{dk_1(E)}}{\mathrm{k_{-1}}}}{1+\frac{k((E)}{k_{-1}[\mathrm{M}]}} \tag{384}$$

Overall k_{uni} will be

$$k_{\text{uni}} = \int_{E_0}^{\infty} \frac{k(E)dk_1(E)/k_{-1}}{1+\frac{k((E)}{k_{-1}[\mathrm{M}]}} \tag{385}$$

Now we need to calculate $\mathrm{d}k_1(E)$ and $k(E)$.

In classical RRK we use the same approach as Hinshelwood to find $\mathrm{d}k_1(E)/k_{-1}$; the probability that a collection of s oscillators has energy between E and E + dE is

$$\mathrm{P(E)dE} = \frac{1}{\mathrm{(s-1)!}}\left(\frac{\mathrm{E}}{\mathrm{k_B T}}\right)^{\mathrm{s}-1} \exp\left(-\frac{\mathrm{E}}{\mathrm{k_B T}}\right)\frac{\mathrm{dE}}{\mathrm{k_B T}} \tag{386}$$

(Integrating this expression from E_0 to ∞ and approximating $E_0 \gg k_B T$ gives the same formula as before for $P(E > E_0.)$)

Now

$$\frac{dk_1(E)}{k_{-1}} = \frac{1}{(s-1)!}\left(\frac{E}{k_B T}\right)^{s-1} \exp\left(-\frac{\mathrm{E}}{\mathrm{k_B T}}\right)\frac{\mathrm{dE}}{\mathrm{k_B T}} \tag{387}$$

Now we need to calculate $k(E)$, the first-order rate constant for decay of A*$(E, E+dE)$.

Important assumption: vibrational energy in the molecule distributes itself statistically through the molecule in a time short compared to $1/k(E)$.

This assumption is called "fast IVR" and has been the subject of much discussion.

To find $k(E)$, think of the molecule as a collection of oscillators. The energy in the molecule gets "reshuffled" once per vibrational period. After each reshuffling, the probability that an energy $\geq E_0$ lands in one critical oscillator is

$$P = \left(\frac{E-E_0}{E}\right)^{s-1} \tag{388}$$

The average amount of time before that happens is $\tau = \frac{1}{\nu}\frac{1}{P}$, so the rate constant $k(E)$ is

$$k(E) = \tau^{-1} = \nu P = \nu\left(\frac{E-E_0}{E}\right)^{s-1} \tag{389}$$

Figure 34:

With our expressions for $dk_1^{(E)}/k_{-1}$ and $k_2(E)$, we calculate k_{uni}:
Define ω = collision frequency = k_{-1}[M], $x = \frac{E-E_0}{RT}$, $b = \frac{E_0}{RT}$, $dx = \frac{dE}{RT}$
Use

$$k_{\text{uni}} = \int_{E_0}^{\infty} \frac{k(E)(dk_1(E)/k_{-1})}{1 + \frac{k(E)}{k_{-1}[\text{M}]}} \tag{390}$$

to get

$$k_{\text{uni}} = \frac{\nu e^{-b}}{(s-1)!} \int_0^{\infty} \frac{x^{s-1}e^{-x}dx}{1 + \frac{\nu}{\omega}\left(\frac{x}{b+x}\right)^{s-1}} \tag{391}$$

That is the "classical RRK theory rate coefficient".
The integral is difficult analytically but easy numerically.

We must estimate	ν	("average" vibrational frequency)
	ω	(collision frequency)
	E_0	(typically high-P activation energy)
	S	(effective number of oscillators)

At high pressures ($\omega \rightarrow \infty$),

$$\int_0^{\infty} x^{s-1}e^{-x}dx = \Gamma(s) = (s-1)! \tag{392}$$

so that

$$k_{\text{uni}} \approx \nu e^{-E_0/RT} \tag{393}$$

Generally, ν and E$_0$ are set to the experimental A and E$_a$ obtained at high pressure. Using the gas kinetic ω, then measuring $p_{1/2}$ and adjusting s to fit it, usually gives a decent representation of the whole falloff curve.

Figure 35:

Figure 36:

4) Quantum RRK. Rather than using the classical expression for the probability that the critical oscillator contains an energy $> E_0$, take a quantum counting expression:

$$k(E) = \nu \frac{(j!)(j-m+s-1)!}{(j-m)!(j+s-1)!} \tag{394}$$

Figure 37:

j = total number of quanta available = E/hv
m = number required in critical oscillator for reaction = E_0/hv
For dk_1/k_{-1}, use quantum stat mech

$$\begin{aligned} P(E_i) &= \frac{g_i e^{-E_i/k_B T}}{\sum_i g_i e^{-E_i/k_B T}} = \frac{g_i e^{-E_i/k_B T}}{Q} && (395)\\ j &= E_i/k_B T && (396)\\ Q &= (1-e^{-hv/k_B T})^{-s} && (397)\\ g_i &= \text{number of ways to distribute j quanta among s oscillators} && (398)\\ &= \frac{(j+s-1)!}{(j!)(s-1)!} && (399) \end{aligned}$$

so

$$\frac{dk_1(E_i)}{k_{-1}} = \left(1-\exp\left(-\frac{\mathrm{hv}}{\mathrm{k_B T}}\right)\right)^s \frac{(j+s-1)!}{j!(s-1)!} e^{-E_i/kBT} \tag{400}$$

Since the E_i are now discrete, we sum to get k_{uni} rather than integrate:

$$\frac{k_{\text{uni}}}{k_\infty} = \left(1-e^{-\frac{hv}{k_B T}}\right)^s \sum_{j=m}^{\infty} \left(\frac{e^{-(j-m)\frac{hv}{k_B T}} \frac{(j-m+s-1)!}{(j-m)!(s-1)!}}{1+\frac{\nu}{\omega}\frac{(j-m+s-1)!j!}{(j+s-1)!(j-m)!}} \right) \tag{401}$$

We need values for ν, ω, s, m.

Set s = 3N-6
ν = exptl. high-pressure A factor
m = E_a^∞/hv
ω = gas-kinetic value

Generally this fits as well or better than classical RRK, with one *less* adjustable parameter. The calculation is also easier.

The RRK theories are generally useful for fitting, interpolation, and explanation of data, but not for any real predictive power.

11.4 Overview of RRKM theory

"RRKM theory" (Rice, Ramsperger, Kassel, Marcus) is another name for microcanonical TST applied to unimolecular reactions. It improves the earlier RRK theories in two ways:

1. Allow a realistic set of vibrational frequencies
2. Use microcanonical TST to evaluate $k_2(E)$ (usually written simply $k(E)$ in this context.)

The "standard" reference books for unimolecular reactions are Robinson & Holbrook and Gilbert & Smith.

The fundamental expressions in RRKM theory are

$$k(E) = \frac{G^{\ddagger}(E - E_0)}{hN(E)} \tag{402}$$

$$\frac{dk_1}{k_{-1}} = \frac{N(E_r)}{Q_r} e^{-E_r/k_B T} \frac{N(E_v)}{Q_v} e^{-E_v/k_B T} dE_r dE_v \tag{403}$$

The first is the microcanonical TST expression I showed before, and the second is the ordinary statistical mechanics equilibrium expression for the probability of a molecule having its internal energy within a particular range, when the molecule's internal states are properly described with quantum mechanical energy levels. Equation 11–67 in SFH gives an approximate result for k_{uni} that arises from these two equations.

To evaluate $k(T)$ we need E_0, $E^{\ddagger}$, $L^{\ddagger}$, vibrational frequencies and moments of inertia for A and $\text{A}^{\ddagger}$, and T. The temperature enters only in the excitation step for a thermal unimolecular reaction. If the molecules are prepared for reaction by a means other than thermal gas-phase collisions (for instance by laser excitation), then the dk_1/k_{-1} part of the calculation is unnecessary and $k(E)$ can be used directly.

Generally RRKM calculations are handled with computer programs, because evaluating the sums and densities of states is tedious for most molecules at the energies relevant to unimolecular reactions. In addition, if thermal rate coefficients are needed, the averaging over internal energies E is best done numerically. Modern treatments also handle the exchange of energy between rotational (useless for reaction) and vibrational energy. (In an isolated polytomic molecule, total energy E and total angular momentum J are strictly conserved, but the distribution of the total energy between vibration and rotation can change with time.)

There is an old but widely used RRKM program available through the Quantum Chemistry Program Exchange at the University of Indiana. A more modern program that follows the approach described in the book by Gilbert and Smith (on reserve) is UNIMOL, available at the Computational Chemistry List archive (`http://www.ccl.net/cca/software/SOURCES/FORTRAN/unimol/`).

Absolute reaction rates may be predicted with RRKM in a manner similar to that described for TST of bimolecular reactions: evaluate reaction barriers, vibrational energy levels, and molecular structure with *ab initio* calculations and plug them into the RRKM formulas. Accuracy similar to that achieved with TST is common.

If high-pressure rate data are available, and the intent is to model the falloff behavior, the most common procedure is to use the high-pressure activation energy to obtain E_0, and use *ab initio* results only for the densities of states. This procedure often gives excellent agreement with experimental results, since it avoids the typical errors of a few kJ/mol in *ab initio* determinations of reaction barriers.

The version of RRKM theory I have described applies to reactions with barriers, as in the top panel of Figure 38. For barrierless dissociations, *variational* TST is required; it requires more input (usually from calculations) but works well. Stephen Klippenstein of case Western Reserve has recently been one of the main developers of this approach. See Gilbert & Smith.

Figure 38:

RRKM can also be used to study other kinds of unimolecular reactions than ordinary thermal collisionally activated ones. “Chemical activation” uses a bimolecular reaction to form a single “hot” product at low pressures. Typically the product will undergo unimolecular reaction before a collisional stabilization takes place. In infrared multiple photon dissociation (IRMPD), CO_2, Nd:YAG, and similar IR lasers dump a pile of IR photons into a strongly absorbing molecule. The resulting unimolecular reaction can usually be described by RRKM.

A fundamental assumption of RRKM is that internal vibrational redistribution (IVR) - random flow of vibrational energy in the molecule - is rapid compared to the timescale of unimolecular reaction. This assumption underlies the use of statistical calculatoin of the rate of passage over the barrier, and is the unimolecular equivalent of the "all internal states of reactants are in Boltzmann equilibrium" in ordinary TST. RRKM also makes all the same assumptions as TST in describing the step $\mathrm{A}^* \longrightarrow \mathrm{A}^{\ddagger}$.

Lifetimes in RRKM are exponential (first-order kinetics.) The most common apparent deviations from RRKM are reactions occurring on excited states which are repulsive; dissociation then occurs on a time scale comparable to 1 vibrational period, and the assumptions of RRKM are not reasonable.

12 Reactions in Solution

What might be different about a reaction occurring in solution (as opposed to the gas phase)?

Collisions - molecules don't move about freely, but solvent is in the way
Energetics - interactions with solvent molecules can dramatically affect equilibrium constants and other properties of reactions. Solvent molecules can break symmetries, etc.
Dynamics - Collisions with solvent maintain thermal equilibrium (in local regions) very effectively. Solvent molecules may play active roles in reactions.

First let's consider the simple problem of collisions. In the gas phase, all we needed was kinetic theory of gases. In solution, we need to pay attention to transport properties, even in well-mixed solutions.

12.1 Cage Effect

Experiment: put 100 black marbles and 2 white marbles in a tray that could hold a maximum of 150 marbles in a single layer. Start shaking the tray. Note the time each time the white marbles collide.

Figure 39:

The average number of collisions per second is about the same as in the gas phase, but the distribution is different. The solvent molecules form a "cage" around the colliding A-B pair, forcing them to undergo several collisions before separating. Each "group" of collisions is called an *encounter*. Reactions that happen very fast, and therefore on the first collision in each encounter, will be slower in solution because the effective number of collisions is reduced to the number of encounters. Those are called "diffusion limited" reactions.

12.2 General Treatment of Transport Effects on Solution Reactions

Reactants move through well-mixed solutions by diffusion and by conduction (electrically driven motion). It is not too difficult to write down a formula that shows the effects of diffusion and conduction on solution reactions. SFH section 4.2 derives a “general phenomenological expression” for the rate constant of a solution reaction, using the following ideas:

1. Diffusion of A and B molecules through the solution, with diffusion constants D_A and D_B, are driven by concentration gradients of [B] around A molecules.

2. Conduction of B molecules (ions) toward or away from A molecules is due to a potential energy of interaction between them, called $V(r)$.

3. There is an “encounter rate coefficient” k_r, the rate coefficient for the “true” concentration of B near the A molecules (at the “critical distance” R). k_R is defined by

$$-\frac{d[\mathrm{B}]}{dt} = k[\mathrm{A}][\mathrm{B}] = k_R[\mathrm{A}][\mathrm{B}](R). \tag{404}$$

The result of their treatment is eqn. 4–24, on p. 130:

$$k = \frac{4\pi(D_A + D_B)\beta}{1 + \frac{4\pi(D_A+D_B)\beta}{k_R e^{-V(R)/k_B T}}} \tag{405}$$

where

$$\beta = \left[\int_R^\infty \frac{e^{V(r)/k_B T}}{r^2} dr\right]^{-1}, \tag{406}$$

and $V(r)$ is the potential energy of interaction of A and B ions at separation r in the solution. Several limiting-case forms of this phenomenological expression are useful in examining solution data.

12.2.1 Diffusion-limited rate coefficient

If the reaction occurs very fast once the reactants have come together, then diffusion of the reactants through the solution is the process that limits the rate. Let us estimate the rate constant in that case and compare it to that for a fast gas phase reaction. Setting $k_R = \infty$ in Eq. (405) gives immediately

$$k_D = 4\pi(D_A + D_B)\beta \tag{407}$$

For neutral molecules, $V(r) = 0$. Then

$$\beta = \left[\int_R^\infty \frac{dr}{r^2}\right]^{-1} = R, \tag{408}$$

so that

$$k_D = 4\pi(D_A + D_B)R. \tag{409}$$

How does this compare with very fast ("gas kinetic") reactions in the gas phase, where the rate is

$$k_{\text{GK}} = \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}} \pi d_{AB}^2? \tag{410}$$

Typical diffusion constants at 300 K are on the order of $10^{-5}\,\text{cm}^2\,\text{s}^{-1}$. If we take both the critical distance R in the solution phase and the hard sphere diameter d_{AB} in the gas phase as 5 Å, and use a reduced mass μ of 30 amu, we find

$$k_D = 1 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} = 8 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1} \tag{411}$$

$$k_{\text{GK}} = 3.6 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} = 2 \times 10^{11}\,\text{M}^{-1}\,\text{s}^{-1} \tag{412}$$

so that a collision-limited gas phase reaction goes about 30 times faster than the same reaction in solution. The factor of 30 difference represents the typical number of collisions in an encounter. For a no-barrier reaction, only the first one counts.

For ions, we must evaluate β in order to estimate the diffusion-limited rate coefficient. The potential energy of interaction is

$$V(r) = \frac{z_A z_B e^2}{\epsilon r} \tag{413}$$

where ϵ is the solvent permittivity, with units $\text{F}\,\text{m}^{-1}$. ϵ is related to the dimensionless dielectric constant ε by the relation $\epsilon = 4\pi\epsilon_0\varepsilon$; ϵ_0 is the permittivity of vacuum, $\epsilon_0 = 8.854188 \times 10^{-12}\,\text{F}\,\text{m}^{-1}$.

(In problems involving electrostatic quantities, I find it useful to remember that the energy stored on a capacitor is given by $E = \frac{1}{2}CV^2$, while power is related to voltage and current by $P = V \cdot I$. These formulas help me remember the relations among the units farad, volt, ampere, and watt.)

Then

$$\beta = \frac{-z_A z_B r_0}{1 - \exp(\frac{z_A z_B r_0}{R})} \tag{414}$$

where

$$r_0 = \frac{e^2}{\epsilon k_B T} \tag{415}$$

r_0 has the value 7 Å at 25° for water, which has $\varepsilon = 78.5$.

For a given R (critical distance of approach), the diffusion-limited rate constant then varies with the product of reactant charges $z_A z_B$, as shown in Table 6 (from SFH).

Table 6

12.2.2 Viscosity effects

The Stokes-Einstein relation describes how the diffusion constant changes with solvent viscosity:

$$D = \frac{k_B T}{6\pi r \eta(T)} \tag{416}$$

where the viscosity $\eta(T)$ has units $\mathrm{kg\,m^{-1}\,s^{-1}}$, and r is the particle radius. For most liquids,

$$\eta(T) \sim e^{+E_\eta/RT} \tag{417}$$

so that

$$D \sim \frac{k_B T}{6\pi r} e^{-E_\eta/RT} \tag{418}$$

and the diffusion-limited rate coefficient will have an apparent activation energy $E_a^{\mathrm{visc}} = E_\eta + RT$.

12.3 Effect of Solvent Dielectric Constant on Slow Reactions Between Ions

For slow reactions, $k_R \ll 4\pi(D_A + D_B)\beta$, and the general solution rate constant expression becomes

$$k = k_R e^{-V(R)/k_B T} \tag{419}$$

$$= k_R \exp\left(\frac{-z_A z_B e^2}{4\pi\epsilon_0 \varepsilon R k_B T}\right) \tag{420}$$

In this expression, only k_R and R are not known. It is sometimes possible to measure the rate of an ionic reaction in a mixed solvent whose dielectric constant ε can be changed by altering the mole fractions of the solvent components. A plot of the logarithm of the obtained k vs. $1/\varepsilon$ should then yield a value of R. Figure 40 shows an example.

Figure 40:

12.4 Effect of Ionic Strength on Reactions Between Ions

Rate coefficients for ionic reactions can be affected by simply adding inert salts to the solutions. This effect can be understood in terms of the shielding effect of the "ion atmosphere" which surrounds a solvated ion in solution. It is similar to, but more drastic than, the reduction of attraction and repulsion by the dielectric constant of the solvent.

The effect of screening by an ion atmosphere is described by Debye-Huckel theory. In a NaCl solution, ion B$^-$ tends to have Na$^+$ around it. The "ion atmosphere" of positive charges "screens" other ions from the potential of B$^-$. The Debye-Huckel expression for the screened potential in a dilute ionic solution is

$$V(r) = \frac{z_A z_B e^2}{\epsilon r} e^{-br}, \tag{421}$$

where the fraction might be called $V_0(r)$ and $1/b$ is the "screening length", given by

$$b^2 = \frac{4\pi e^2}{\epsilon k_B T} \sum_i c_i^0 z_i^2, \tag{422}$$

where c_i^0 is the bulk concentration of species i. The *ionic strength* is

$$I = \frac{1}{2} \sum_i m_i z_i^2, \tag{423}$$

where m_i is the molal concentration of species i. If we assume that the volume of 1 kg of solvent does not change when the salt is added (the mass certainly does), then

$$\sum_i c_i^0 z_i^2 = 2I\rho N_0 \tag{424}$$

where ρ is the density of the *solvent* (not solution as SFH say), and N_0 is Avogadro's number. So

$$b^2 = \frac{8\pi e^2 \rho N_0 I}{\epsilon k_B T} \tag{425}$$

Since $e^{-br} \sim 1 - br$ for small br, we can evaluate β from

$$\begin{aligned} V(r) &= V^0(r)(1 - br) = V^0(r) - z_A z_B r_0 b k_B T & (426) \\ \beta^{-1} &= \int_R^\infty \frac{e^{(V^0(r) - z_A z_B r_0 b k_B T)/k_B T}}{r^2} dr & (427) \\ &= e^{-z_A z_B r_0 b} \int_R^\infty \frac{e^{-V^0(r)}/k_B T}{r^2} & (428) \\ \beta &= e^{-z_A z_B r_0 b} \beta^0 & (429) \end{aligned}$$

Using Eq. (426) and Eq. (429) in the general expression for the solution rate coefficient (Eq. (405)) gives (try it!)

$$k = k^0 \exp(z_A z_B r_0 b) \tag{430}$$

k^0 is the rate constant at infinite dilution, when $\beta = \beta^0$.

Since $b \propto \sqrt{I}$, a plot of $\ln k$ vs. $\sqrt{I}$ should be a straight line.

$$\begin{aligned} \log_{10} k &= \log_{10} k^0 + \frac{z_A z_B r_0 b}{2.303} && (431) \\ &= \log_{10} k^0 + \frac{z_A z_B e^2}{(2.303)\epsilon k T} \left(\frac{8\pi e^2 \rho N_0}{\epsilon k_B T} \right)^{1/2} I^{1/2} && (432) \end{aligned}$$

For water at 298 K, $\rho = 997\,\mathrm{kg\,m^{-3}}$ and $\epsilon = 78.5$, so

$$\log_{10} k = \log_{10} k^0 + 1.02 z_A z_B I^{1/2} \tag{433}$$

Like the dielectric constant, the effect of ion atmosphere screening is to reduce the effect of the long-range Coulomb forces between reacting ions. Reactions between charged ions are speeded up and reactions between oppositely ions are slowed down.

This *primary salt effect* can be used to find the charge product $\mathrm{z_A z_B}$ for the rate limiting step of a reaction whose mechanism is unknown. Examples are shown in the plots from SFH on the next page. Perhaps more important, this analysis shows that in carrying out kinetic studies on charged reactants in solution, it can be important to maintain constant ionic strength in the solution as the reactant concentration is varied, in order to avoid confusing rate coefficient changes due to ionic strength variations with rate chenges due to reactant concentrations. Sodium or potassium perchlorate is commonly added to reaction mixtures for this purpose.

12.5 “Energetic” and “Dynamic” Solvent Effects

In the previous two lectures I outlined the treatment of “collisional” effects of solvents, which affect measured rates primarily by modifying the effective collision rate with respect to the value expected for a gas-phase reaction. That material can be thought of as treating the changes in A-factor brought about by the solvent.

Today, I want to give a mostly qualitative discussion of more intrinsic solvent effects. Interactions of solvent molecules directly with reactants in the encounter complex, either time-averaged (static) or dynamic, are important.

Interactions with solvent always lower the total enthalpy (and, generally, free energy) of solutes. However, the activation energy E_a or threshold energy E_0 can be either increased or decreased by solvation:

Figure 41:

How might we extend TST to account for solvent effects? In the gas phase,

$$k = \frac{k_B T}{h} K_c^{\ddagger} \tag{434}$$

In solution thermodynamics, the equilibrium constant is defined by a ratio of *activities* (not concentrations),

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{435}$$

$$K_{eq} = \frac{a_c}{a_B a_A} = \frac{[\mathrm{C}]\gamma_c}{[\mathrm{A}][\mathrm{B}]\gamma_A \gamma_B} = K_c \frac{\gamma_c}{\gamma_A \gamma_B} \tag{436}$$

The rate coefficient, though, is defined in terms of the *concentration* of a transition state:

$$\mathrm{A}+\mathrm{B} \rightleftharpoons (\mathrm{AB})^{\ddagger} \rightarrow \text{products} \tag{437}$$

$$\text{Rate} = \frac{d[\text{products}]}{dt} = k[\mathrm{A}][\mathrm{B}] = \frac{kT}{h}K_c^{\ddagger}[\mathrm{A}][\mathrm{B}] \tag{438}$$

so

$$k = \frac{k_B T}{h}K_{eq}^{\ddagger}\frac{\gamma_A\gamma_B}{\gamma^{\ddagger}} = K_{ref}\cdot\frac{\gamma_A\gamma_B}{\gamma^{\ddagger}} \tag{439}$$

where $K_{eq}^{\ddagger}$ is the thermodynamic equilibrium constant for formation of the actinated complex. γ_A and γ_B are measurable, but $\gamma^{\ddagger}$ presents a problem.

Saying the same thing in slightly different language,

$$k = \frac{kT}{h}e^{\Delta S_0^{\ddagger}/R}e^{-\Delta H_0^{\ddagger}/RT}\left(c^{\Theta}\right)^{\Delta m^{\ddagger}}\alpha\frac{kT}{h}e^{-\Delta G_0^{\ddagger}/RT} \tag{440}$$

In going from gas phase to solution, or from one solution to another, the $\Delta G_0^{\ddagger}$ might change.

$$\begin{aligned}
k_0 &\propto \frac{kT}{h}\exp\left(-\left(G_0^{\ddagger}-G_0^{reactants}\right)\right) \text{ “reference” rate} && (441)\\
k &\propto \frac{kT}{h}\exp\left(-\left(G^{\ddagger}-G^{reactants}\right)\right) \text{ new rate} && (442)\\
&= k_0\exp\left(-\left(G^{\ddagger}-G_0^{\ddagger}\right)-\left(G^{reactants}-G_0^{reactants}\right)\right) && (443)\\
&= k_0\exp\left(-\left[\left(G^{\ddagger}-G^{reactants}\right)-\left(G_0^{\ddagger}-G_0^{reactants}\right)\right]\right) && (444)\\
&= k_0\exp\left(-\delta\Delta G^{\ddagger}\right) \qquad \text{cf. SFH eq. 12-27} && (445)
\end{aligned}$$

The rate in the “reference” environment gets multiplied by exp(-$\delta\Delta G^{\ddagger}$), where $\delta\Delta G^{\ddagger}$ is the change in Gibbs function of activation.

If the reference environment is the gas phase,

$$\delta\Delta G^{\ddagger} = \Delta G_{solv}^{\ddagger} - \Delta G_{solv}^{reac} = \Delta H_{solv}^{\ddagger} - \Delta H_{solv}^{reac} - T\left(\Delta S_{solv}^{\ddagger} - \Delta S_{solv}^{reac}\right) \tag{446}$$

Solvation enthalpies and entropies are sometimes available in the literature, though it is important to check standard-state conventions carefully. For transition states they are never available (well, almost never.) Generally one can hope only for a qualitative or semiquantitative understanding. If you want to try predictive work, you have several options for estimating $\Delta H_{solv}^{\ddagger}$ and $\Delta S_{solv}^{\ddagger}$:

1) Relation to model compounds, as in gas-phase procedure. Pay particular attention to differences in polarity between model compound and transition state.

2) Create empirical correlations with similar compounds/reactions.

3) Calculate using solvent-solute potentials (not easy; see SFH p. 408).

References on these options:

S.G. Entelis, *Reaction Kinetics in the Liquid Phase*, Helsted Press, NY (1976).

S.W. Benson and D.M. Golden, in *Physical Chemistry, An Advanced Treatise*. Volume VVI. Reactions in Condensed Phases. H. Eyring, editor. Academic, NY (1975) p. 58.

E. Buncel and H. Wilson, Acc. Chem. Res. *12*, 42 (1979).

E. Buncel and H. Wilson, J. Chem. Ed. *57*, 629 (1980).

C. Reichardt, *Solvent Effects in Organic Chemistry*, Verlag Chemie, Weinheim and New York, 1979.

(list from M. Kreevoy and D. Truhlar, in *Investigation of Rates and Mechanisms of Reactions*, 4th ed., ed. by C. Bernasconi (Wiley)).

There is a fair amount of research activity devoted to developing improved TST models of energetic solvent effects. Several of the current "solvation models" are already available in "canned" form in the POLYRATE program. A bibliography of papers describing these models is available at `http://comp.chem.umn.edu/solvation/solref.html`

The initial package was described in JACS *113*, 8305 (erratum: *113*, 9901) The most recent model is described in Chem. Phys. Lett. *288*, 293 (1998).

The main authors of these papers are Chris Cramer and Donald Truhlar of the University of Minnesota.

12.6 Hughes-Ingold approach

The classic treatment of solvation is the Hughes-Ingold approach, described in

- C.K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd ed., Cornell Univ. Press, Ithaca, NY 1969;
- A.J. Parker, Chem. Rev. *69*, 1 (1969).
- E.D. Hughes and C.K. Ingold, J. Chem. Soc. 244 (1935).

Consider the following figure. The transition state is more polar than the reactants; a polar solvent will have stronger interactions with the TS than the reactants and $\Delta G^{\ddagger}$ will be lower (so the rate higher) in more polar solvents.

Reactions with transition states that are less polar than reactants will generally show the opposite effect. Neutralization reactions between ions are an example.

In thinking about solvent-transition state interactions, it is useful to remember the *Hammond postulate*: the transition state for an elementary step will more closely resemble the stable state(reactants or products) which is closest to it in energy.

An *endothermic* reaction will have a transition state which resembles the products. An exothermic reaction will have a transition state which resembles the reactant.

Figure 42:

This idea is given quantitative meaning in several different contexts, including the large fields of "linear free energy relationships" and Marcus theory.

13 Linear Free Energy Relationships

"LFER" are empirical correlations observed between rate coefficients or rate and equilibrium coefficients, usually among reactions within a series of similar mechanism.

Nothing makes these correlations *necessary*. They are a semiquantitative way of "systematizing" chemist's ideas about the similarity of reactions. The most useful examples are the ones with well-defined domains of applicability, including the Hammett equation and the Bronsted catalysis law.

My general advice:

Correlations which apply to well-defined groups of reactions, and which use primary data (such as measured rate and equilibrium constants) can be very useful. Two good references are Connors' kinetics book (on reserve) and *Correlation Analysis in Chemistry*, N.B. Chapman and J. Sharler, eds., (plenum, 1978).

Correlations among derived quantities, such as enthalpies and entropies obtained from rate or equilibrium constants, or activation energies and A factors, should be regarded with strong skepticism. In particular, most discussions of "kinetic compensation" are useless.

Figure 43:

Most LFERs take the form of relations among rate or equilibrium constants along a reaction series.

For example:

$$\ln k = m \ln K_c + b \tag{447}$$

The plot of $\ln k$ vs. $\ln K_c$ would be made for a series of similar reactions.

Since

$$\ln k = \ln\left(\frac{kT}{h}\right) - \frac{\Delta G^{\ddagger}}{RT} \tag{448}$$

and

$$\ln K_c = -\frac{\Delta G^0}{RT} \qquad \text{(times a pressure-to-concentration factor),} \tag{449}$$

$$\Delta G^{\ddagger} = m' \Delta G^0 + b'. \tag{450}$$

These are “extrathermodynamic relationships” - they are not necessary but are relatively common.

The utility is that if rates are measured for some reactions in a series, and equilibrium constants for all, the rates for the remaining ones can be estimated. A common application in organic chemistry is prediction of rates in series of reactions with the same mechanism.

13.1 Hammett equation

The most famous example of an LFER is the Hammett equation:

$$\log_{10}\left(\frac{k}{k^0}\right) = \rho\sigma, \tag{451}$$

where k is the rate coefficient for some reaction of a substituted aromatic compound, and k^0 is the rate for the same reaction of an unsubstituted compound. σ is the “substituent constant”, defined for a particular aromatic ring substituent as

$$\sigma = \log_{10} \frac{K_a}{K_a^0} \tag{452}$$

where K_a^0 is the acid dissociation constant for ordinary benzoic acid and K_a is the acid dissociation constant for benzoic acid with the substituient of interest. A given substituent will have different σ for the *meta* and *para* positions. ρ is the “reaction constant”, obtained by making rate measurements on several reactions with different substituents and setting ρ equal to the slope of a plot of $\log_{10} k$ vs. σ. ρ varies not only with reaction type but also with solvent.

The following page gives a table of σ and ρ values for several substituents and reactions. As an example, let us predict the rate of

(453)

σ for m-CH_2CH_3 is -.07, and ρ for base-catalyzed hydrolysis of esters is 2.229, with $\log_{10} k^0 = -2.075$. So we have

$$\log_{10}\left(\frac{k}{k^0}\right) = \sigma\rho \tag{454}$$

$$k = k_0 10^{\sigma\rho} = 10^{-2.075} 10^{(-0.7)(2.229)} \tag{455}$$

$$= 5.87 \times 10^{-3}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1} \tag{456}$$

The Hammett equation only works for *m*- and *p*- substituted aromatics.

Other LFERs include the Taft equation, which is like Hammett but for aliphatic compounds, the Swain-Scott equation for nucleophilic substitution, and the Bronsted acid catalysis law.

13.2 The Marcus Equation

"Marcus theory" describes a quadratic free energy relationship. It is a semiempirical theory intended mostly to correlate solution reaction rates for electron transfer. It has been extended, with considerable success, to atom, proton, hydride, and group transfers as well.

The "reaction coordinate" includes both changes in internal structure of the donor (D) and acceptor (A) complexes, and motion of the solvent molecules. The simple version of Marcus theory we shall describe assumes that it is useful to define the reaction coordinate x so that the two free energy curves, for $\mathrm{D} + \mathrm{A}$ and for $\mathrm{D}^+ + \mathrm{A}^-$, are parabolas with minima at x_R and x_P, and that the "force constant" f is the same in both the reactant and product wells.

With these assumptions we want to find a relation between $\Delta G^\ddagger$ and ΔG^0. At the TS, G_R and G_P are equal:

$$\frac{1}{2} f (x_{\mathrm{TS}} - x_R)^2 - \Delta G^0 = \frac{1}{2} f (x_{\mathrm{TS}} - x_P)^2 \tag{457}$$

Define $\Delta x = x_P - x_R$. Then

$$\frac{1}{2} f (x_{\mathrm{TS}} - x_R)^2 - \Delta G^0 = \frac{1}{2} f (x_{\mathrm{TS}} - (\Delta x + x_R))^2 \tag{458}$$

Expand, cancel terms, and solve for x_{TS}:

$$x_{\mathrm{TS}} = x_R + \frac{\Delta x}{2} + \frac{\Delta G^0}{f \Delta x} \tag{459}$$

Figure 44: Reaction coordinate diagram for electron transfer with definitions of Marcus parameters.

We have now "found" the location of the transition state for a given ΔG^0. If $\Delta G^0 = 0$ (for a symmetric reaction), $x_{\text{TS}} = \frac{x_R + x_P}{2}$. As ΔG^0 becomes more negative, x_{TS} looks more and more like x_R; this is a quantititave version of the Hammond postulate.

Now use this value of x_{TS} to find $\Delta G^\ddagger$.

$$\Delta G^\ddagger = \frac{1}{2} f (x_{\text{TS}} - x_R)^2 \tag{460}$$

$$= \frac{1}{2} f (x_R + \frac{\Delta x}{2} + \frac{\Delta G^0}{f \Delta x} - x_R)^2 \tag{461}$$

$$= \frac{1}{2} f \left(\frac{\Delta x}{2} \right)^2 \left(1 + \frac{2 \Delta G^0}{f \Delta x^2} \right)^2 \tag{462}$$

Define the "reorganization energy" λ:

$$\lambda = \frac{1}{2} f (\Delta x)^2 \tag{463}$$

Then

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{0}}{\lambda}\right)^{2} \tag{464}$$

which is the Marcus equation.

If $\Delta G^{0} = 0, \Delta G^{\ddagger} = \frac{\lambda}{4}$. $\frac{\lambda}{4}$ is called the intrinsic barrier.

This equation relates rate and equilibrium constants for series of reactions. In the simplest application, we measure $\Delta G^{\ddagger}_{BB}$ for a symmetric reaction

$$\mathrm{B}^{-} + \mathrm{B} \rightarrow \mathrm{B} + \mathrm{B}^{-} \tag{465}$$

(for instance from nmr lineshapes for proton exchange). We make the same measurement for the other symmetric reaction

$$\mathrm{A}^{-} + \mathrm{A} \rightarrow \mathrm{A} + \mathrm{A}^{-} \tag{466}$$

to get $\Delta G^{\ddagger}_{AA}$. Then for the reaction

$$\mathrm{B}^{-} + \mathrm{A} \rightarrow \mathrm{B} + \mathrm{A}^{-}, \tag{467}$$

we calculate

$$\lambda_{AB} = \frac{\lambda_{BB} + \lambda_{AA}}{2} \tag{468}$$

$$= 4\frac{(\Delta G^{\ddagger}_{BB} + \Delta G^{\ddagger}_{AA})}{2} \tag{469}$$

and then

$$\Delta G^{\ddagger}_{AB} = \frac{\Delta G^{\ddagger}_{AA} + \Delta G^{\ddagger}_{BB}}{2}\left(1 + \frac{\Delta G^{0}_{AB}}{\lambda}\right)^{2} \tag{470}$$

So, in a reaction series, if we can measure the kinetics for all the symmetric reactions, and measure or look up ΔG^{0} for the unsymmetric ones, we can calculate $\Delta G^{\ddagger}$ for the unsymmetric reactions. This gets us $n(n-1)$ rate coefficients in a series of n different reactants. Several other forms of this equation (sometimes called the "Marcus cross relation") are also used; see Espenson for some examples.

13.3 The inverted region

Note that the most basic Marcus expression,

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{0}}{\lambda}\right)^{2} \tag{471}$$

makes a very interesting prediction: as the reactions become more exothermic, the rate will increase *until* $\Delta G^0 = -\lambda$. Beyond that, the rate will begin to decrease again.

The effect is easy to understand graphically; the idea is illustrated in Figure 45. In the "inverted" region, the solvent must move *away* from the equilibrium product configuration in order to allow an energetically neutral electron transfer.

Figure 45:

The existence of this inverted region, now well accepted, was in dispute until about 1986. One confirming set of data is shown in Figure 46.

Figure 46:

14 Reactions on Surfaces

Heterogeneous catalysis is a 2×10^9 /yr industry in the US, and most of it is done with solid catalysts.

An important distinction: "adsorption" implies molecules sitting on a surface, while "absorption" implies molecules inside the bulk solid structure.

Molecules can be adsorbed with various strengths, but two broad classes are generally recognized.

Physisorption weak bonds caused by van der Waals interactions join surface atoms and adsorbate. Binding energies are low ($\lesssim 20$ kJ/mol), surface-molecule distances are large ($\sim 4 - 10$ Å), and there is only a small overlap between surface orbitals and orbitals on adsorbed species.

Chemisorption - there is a chemical interaction between surface atoms and adsorbed species. Binding energies are $200 - 500$ kJ/mol, surface-molecule distances are those of normal chemical bonds (1–3 Å), and there is large overlap between surface and adsorbate orbitals.

In some systems and experiments there appears to be a clear barrier between physisorption and chemisorption wells.

Figure 47:

Molecules adsorb on "sites". Typically chemisorption is more important for catalysis. Sites can be

- Individual surface atoms in smooth planes ("terraces")
- Atoms at steps, kinks, or vacancies
- Spaces between 2 or 3 surface atoms ("bridge" sites)

14.1 Langmuir isotherm

Here I develop a simple model of adsorption equilibrium.

Catalyst has a number S_0 of sites per unit area. We define the *coverage* θ as the fraction of those sites which are occupied by adsorbate molecules:

$$\theta = \frac{\text{\# of A-S pairs per unit area}}{S_0} \tag{472}$$

If the molecules can "pile up", θ can have any value from 0 to ∞; if they can only adsorb on unoccupied sites, $0 \le \theta \le 1$. Assume the latter for the moment. Consider the reaction

$$\mathrm{A} + \mathrm{S} \underset{\mathrm{k_{-a}}}{\overset{\mathrm{k_a}}{\rightleftharpoons}} \mathrm{AS} \tag{473}$$

It's a little hard to define [S], but the rate of adsorption should be proportional to the number of A-S collisions, so say

$$\mathrm{Rate}_{\rightarrow} = k_a[\mathrm{A}](1-\theta) \tag{474}$$

$$\mathrm{Rate}_{\leftarrow} = k_{-a}\theta \tag{475}$$

At equilibrium $k_{-a}\theta = k_a[\mathrm{A}](1-\theta)$

$$K_{ads} = \frac{k_a}{k_{-a}} = \frac{\theta}{[\mathrm{A}](1-\theta)} \tag{476}$$

the "Langmuir isotherm", also written as

$$\theta = \frac{K_{ads}[\mathrm{A}]}{1+K_{ads}[\mathrm{A}]} \tag{477}$$

If our mechanism looks like

$$A + S \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} AS \xrightarrow{k_2} P, \tag{478}$$

then

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{AS}] = k_2\theta S_0 \tag{479}$$

The L. isotherm gives

$$\theta = \frac{K_{ads}[\mathrm{A}]}{1+K_{ads}[\mathrm{A}]}, \tag{480}$$

so

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_2 K_{ads} S_0 [\mathrm{A}]}{1 + K_{ads}[\mathrm{A}]} \tag{481}$$

At low [A], this looks 1st-order in A. At high [A], it's zero-order in A. The behavior is similar to that found in enzyme kinetics. If a finite number of active sites is available, a saturation behavior is observed in either case.

Figure 48:

Since metal catalysts are purchased by weight, and only their surfaces are active, they are usually very finely divided in order to maximize the surface-to-volume ratio.

The assumptions made in this derivation included the following:

1. No interactions among molecules (AS → AS or A → AS)
2. Single layer coverage only
3. All surface sites are equivalent.

If molecules dissociate on the surface,

$$\mathrm{A}_2 + 2\mathrm{S} \rightleftharpoons 2\mathrm{AS} \tag{482}$$

$$\mathrm{rate}_{\rightarrow} = k_a [\mathrm{A}_2](1-\theta)^2 \tag{483}$$

$$\mathrm{rate}_{\leftarrow} = k_{-a}\theta^2 \tag{484}$$

At equilibrium,

$$\left(\frac{\theta}{1-\theta}\right)^2 = \frac{k_a}{k_{-a}}[\mathrm{A}] \tag{485}$$

so that

$$\theta = \frac{K_{ads}^{1/2}[\mathrm{A}_2]^{1/2}}{1 + K_{ads}^{1/2}[\mathrm{A}_2]^{1/2}} \tag{486}$$

Now, at low $[\mathrm{A}_2]$, $\theta \sim [\mathrm{A}_2]^{1/2}$.
At high $[\mathrm{A}_2]$,

$$1 - \theta = \frac{1}{1 + K_{ads}^{1/2}[\mathrm{A}_2]^{1/2}} \tag{487}$$

so that at high $[\mathrm{A}_2]$,

$$K_{ads}[\mathrm{A}_2]^{1/2} \gg 1 \tag{488}$$

and

$$1 - \theta = \frac{1}{K_{ads}^{1/2}[\mathrm{A}_2]^{1/2}} \tag{489}$$

This $P^{-1/2}$ dependence of the free sites is characteristic of dissociative chemisorption.

14.2 Kinetics of reactions on surfaces

The basic mechanism of a surface reaction includes 5 steps:

1. Diffusion to surface
2. Adsorption
3. Reaction
4. Desorption
5. Diffusion away

The "Langmuir-Hinshelwood mechanism" treats step 3 as a reaction between two adsorbed molecules. It assumes equilibrium between gas-phase and adsorbed species, and assumes 2) and 4) are fast so 3) is the rate determining step.

For unimolecular reactions, we have

$$\begin{aligned}
\mathrm{A(g)} + \mathrm{S} &\rightleftharpoons \mathrm{AS} \qquad \text{fast} && (490)\\
\mathrm{AS} &\rightarrow \mathrm{XS} \qquad \text{slow} && (491)\\
\mathrm{XS} &\rightleftharpoons \mathrm{X(g)} + \mathrm{S} \qquad \text{fast} && (492)
\end{aligned}$$

With the rapid equilibrium assumption for both A and X, and defining pressure-unit equilibrium constants K_p^A and K_p^X,

$$\frac{dP_x}{dt} = k[\mathrm{AS}] = k'\theta_A = \frac{k'K_p^A p_A}{1 + K_p^A p_A + K_p^X P_X} \tag{493}$$

from the Langmuir isotherm for competitive adsorption.

For large pressure of A, low X coverage, if the reactant is adsorbed strongly and the product weakly, that is,

$$P_A K_p^A \gg 1 + K_p^X P_X, \tag{494}$$

then $\frac{dP_X}{dt} = k'$ and we have zero-order kinetics. The kinetics are (again) controlled by the available number of sites and the time required for A-X to react.

For $P_A K_p^A \ll 1$ and $P_X K_p^X \ll 1$, $\frac{dP_X}{dt} = k'K_p^A P_A$ and the reaction appears first order. Here the kinetics are controlled by the amount of A available to populate the sites.

For $P_X K_p^X \gg 1 + P_A K_p^A$, $\frac{dP_X}{dt} = k'\frac{K_p^A P_A}{K_p^X P_X}$. Here the product refuses to let go of sites, and inhibits the reaction.

For bimolecular reactions we have slightly different behavior.

Assume the Langmuir-Hinshelwood mechanism:

$$\mathrm{A} + \mathrm{S} \rightleftharpoons \mathrm{AS} \tag{495}$$

$$\mathrm{B} + \mathrm{S} \rightleftharpoons \mathrm{BS} \tag{496}$$

$$\mathrm{AS} + \mathrm{BS} \rightarrow \mathrm{XS} + \mathrm{S} \tag{497}$$

$$\mathrm{XS} \rightleftharpoons \mathrm{X} + \mathrm{S} \tag{498}$$

where the third reaction is the rate-determining one, and all equilibria are considered fast (“established”). Then

$$\frac{dP_X}{dt} = k'\theta_A\theta_B = \frac{k'K_p^A P_A K_p^B P_B}{(1 + K_p^A P_A + K_p^B P_B + K_p^X P_X)^2} \tag{499}$$

If P_B is held constant while P_A is varied, the rate passes through a maximum because we need to have both A and B present on the surface.

At low pressure of both A and B, and $P_X K_p^X \ll 1$

$$\text{rate} = k'K_p^A P_A K_p^B P_B \qquad \text{ordinary 2nd order.} \tag{500}$$

If B is adsorbed much more strongly than A,

$$\text{rate} \sim \frac{k'K_p^A P_A}{K_p^B P_B} \tag{501}$$

Figure 49:

Here the reaction is inhibited by B, because it takes up sites needed by A.

Note that the rate at which AS and XS diffuse on the surface is implicitly included in k'.

14.3 Rideal-Eley mechanism

An alternative gas-surface mechanism is the Rideal-Eley one:

$$\mathrm{A} + \mathrm{S} \rightleftharpoons \mathrm{AS} \tag{502}$$

$$(\mathrm{B} + \mathrm{S} \rightleftharpoons \mathrm{BS}) \tag{503}$$

$$\mathrm{B} + \mathrm{AS} \rightarrow \mathrm{XS} \tag{504}$$

$$\mathrm{XS} \rightleftharpoons \mathrm{X} + \mathrm{S} \tag{505}$$

B molecules “divebomb” A stuck to surface. No example of a pure Rideal-Eley reaction is known, though it is certainly possible to have Rideal-Eley steps as parallel processes with the more common reaction between two adsorbed species.