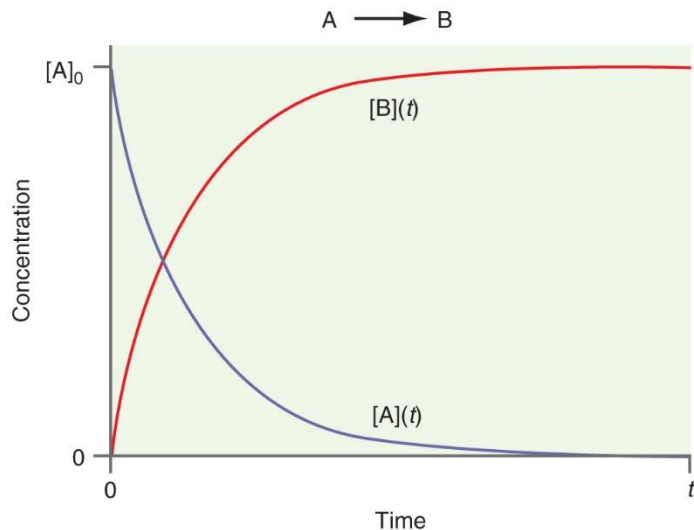Everything above was related to equilibrium, but the changes will always take time. Ice don't melt instantaneously, neither the chemical reactions happen instantaneously. Even in principle everything is in equilibrium, in reality they are not.

The most stable form of carbon and oxygen is CO_2 but not all carbon is in CO_2.

Why? The reactions are slow.

You can have several carbon containing molecules (or yourself) in air at room temperature and they do not burn. If you increase the temperature the situation is different.

We need to consider time (or kinetics). If we look the time behavior of a trivial reaction A → B. The A(t) and B(t) are rather obvious. The long time limit is the equilibrium. (A can be ice and B liquid water at temperature above 0 C)

Next we need to define the **rate of chemical reaction**. That is how many reaction ξ happen in 1 s. This is connected to mole change

$$\frac{dn}{dt} = \nu \frac{d\xi}{dt}$$

The stoichiometric coefficient is needed since in a dissociation reaction on molecule broke and two are formed. The rate is

$$Rate = \frac{d\xi}{dt} = \frac{1}{\nu}\frac{dn}{dt}$$

An example: 4 NO_2 + O_2 -> 2 N_2O_5

$$Rate = -\frac{1}{4}\frac{dn(NO_2)}{dt} = -\frac{dn(O_2)}{dt} = \frac{1}{2}\frac{dn(N_2O_5)}{dt}$$

This definition of rate depend on the system size (the amount of matter, n). To make it an intensive variable it can be divided by the volume of the system.

$$R_i = \frac{Rate}{V} = \frac{1}{\nu_i V}\frac{dn_i}{dt} = \frac{1}{\nu_i}\frac{d[i]}{dt}$$

where [i] is the moles of species i divided by the volume.

The rate of a reaction A + B -> X depend on the concentration [A], [B] etc.

$$R = f([A], [B]) \quad \text{often} \quad R = k[A]^\alpha [B]^\beta$$

this the **rate law**. If it is in the power form the exponents are called **the reaction order**. The rate law need to be determined experimentally.

An example $4 NO_2 + O_2 \rightarrow 2 N_2O_5$

$$R = k[NO_2]^2 [O_2]$$

this reaction is first order with respect of O_2 and second order of NO_2. The total reaction order is 3.

If the rate law is known, then the reaction dynamics can be solved. The simplest case is the unimolecular first order reaction

$$R = -\frac{d[A]}{dt} = k[A]$$

this is a first order differential equation and its solution is [A](t)=A$_0$exp(-kt). The concentration decay exponentially with coefficient k. The k need to be determined experimentally.

if the concentration in the beginning is 1 M (mol/L) and we measure the rate to be 40 M/s. The rate constant k=40 1/s. The rate law can be tested at later time. If at 30 ms the concentration is 0.3 M and the rate is 12 M/s the k(30ms)=R(30 ms)/[A](30 ms)=12/0.3 1/s = 40 1/k. So the rate law is correct and the k is constant.

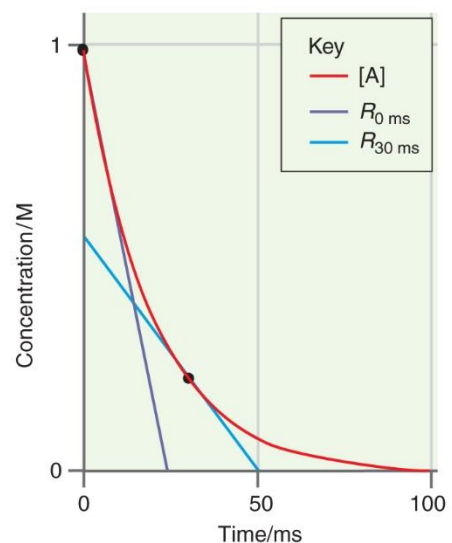The rate law determination is easy. Consider a simple reaction A + B -> C

R = k[A]$^\alpha$[B]$^\beta$

We can use isolation method in which one concentration is much higher than the other and then the major component is essentially not consumed. Choose [B] >> [A] then [B] is almost constant B$_0$.

R = k[A]$^\alpha$[B]$^\beta$ ≈ k B$^\beta$$_0$ [A]$^\alpha$ = k' [A]$^\alpha$ now α is easy to determine. The experiments can be done with reversed conditions, [A] >> [B] and the β can be determined. At 2 different concentrations of [A], [A]$_1$ and [A]$_2$ the ratio of the rates is and taking log of these will give the α

$$\frac{R_1}{R_2} = \frac{k[A]_1^\alpha [B]_0^\beta}{k[A]_2^\alpha [B]_0^\beta} = \left(\frac{[A]_1}{[A]_2}\right)^\alpha \quad => \quad \ln\frac{R_1}{R_2} = \alpha \ln\frac{[A]_1}{[A]_2}$$

Another method is initial rate method. Now concentration of one component is kept constant, the other is varied and the initial rate is measured. The equations are the same as before.

[A]x10^{-4} mol/L	[B] x10^{-5} mol/L	initial rate M/s
2.30	3.10	5.25x10^{-4}
4.60	6.20	4.20x10^{-3}
9.20	6.20	1.68x10^{-2}

$$\frac{R_2}{R_3} = \frac{4.20 * 10^{-3}}{1.68 * 10^{-2}} = \left(\frac{4.6}{9.2}\right)^{\alpha} \quad => \quad \ln\frac{R_2}{R_3} = \alpha \ln\frac{4.6}{9.2} => -1.386 = \alpha * -0.693 => \alpha = 2$$

$$\frac{R_1}{R_2} = \frac{5.25 * 10^{-4}}{4.20 * 10^{-3}} = \left(\frac{2.3}{4.6}\right)^2 \left(\frac{3.1}{6.2}\right)^{\beta} \quad => \quad 0.125 = 0.25 * (0.5)^{\beta} => \beta = 1$$

The equations are quite simple but the measurements of concentration of fast reaction are not easy. Sometimes physical quantities like pressure can be used to follow the reaction. Usually, some spectroscopical methods are convenient. IR adsorption can be measured in ms.

Integrated rate laws	Engel & Reid chapter 35.5

As shown above the time dependence of the reaction components can be solved when the rate law is known. In simple cases the solution can be written with simple function but usually the solution can obtained only numerically.

The first order reaction, A -> P

$$R = -\frac{d[A]}{dt} = k[A] \quad => \quad [A](t) = [A]_o e^{-kt}$$

where the $[A]_0$ is the initial concentration. The product concentration is $[P]+[A]=[A]_0$

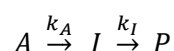and [P](t)= [A]$_0$(1-exp(-kt))

The second order reaction 2A -> P is also easy

$$R = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^2 \quad => \quad \frac{1}{[A](t)} - \frac{1}{[A]_0} = 2kt = k_{eff}t$$

the more general reaction A + B -> P is more complex, see the derivation from the book

$$R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \quad => \quad \frac{1}{[B]_0 - [A]_0}\ln\frac{[A]/[A]_0}{[B]/[B]_0} = kt$$

In chemical reactions there are often intermediate compounds and the total rate of the reaction chain depend on these intermediate steps. In this case, the reaction can be written as

$$A \xrightarrow{k_A} I \xrightarrow{k_I} P$$

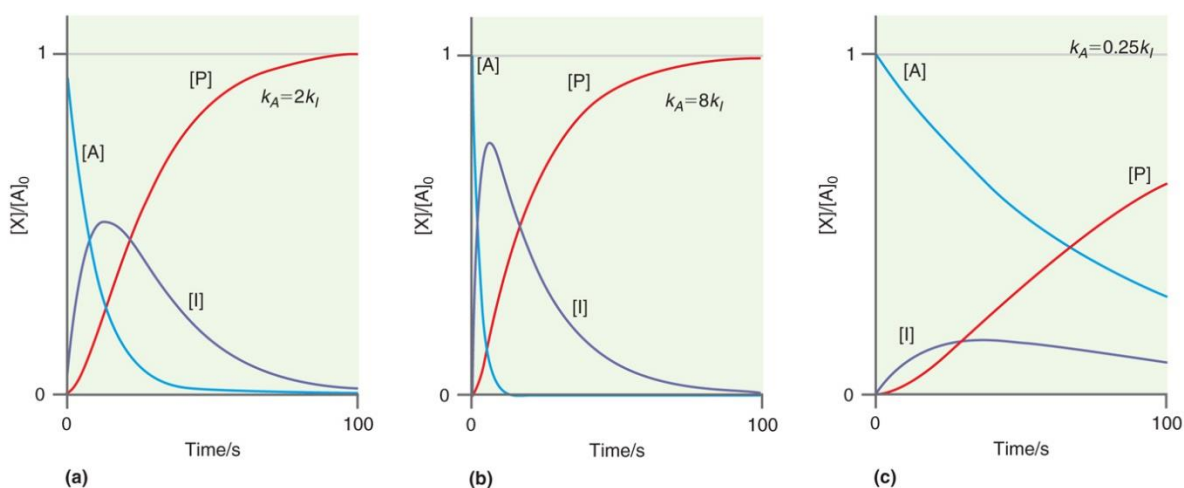Here we are interested the product P. For first order reaction (and no backward reactions) the equations can be written as

$$\frac{d[A]}{dt} = -k_A[A], \quad \frac{d[I]}{dt} = k_A[A] - k_I[I], \quad \frac{d[P]}{dt} = k_I[I]$$

We assume that the initial concentrations of I and P are = 0. The solutions are quite easy

$$[A](t) = [A]_o e^{-k_A t},$$

$$[I](t) = [A]_o \frac{k_A}{k_I - k_A}(e^{-k_A t} - e^{-k_I t}), \quad [P](t) = [A]_o(\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1)$$

With different rate constant, the concentrations are shown below. The intermediate compound concentration is never very high.

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Even this model is very simple it contain many important features of chemical reactions.

The rate limiting step

we can look the time dependence of the product at two limits, a) when $k_A \gg k_I$ and exp(-$k_A t$) << exp(-$k_I t$)   then
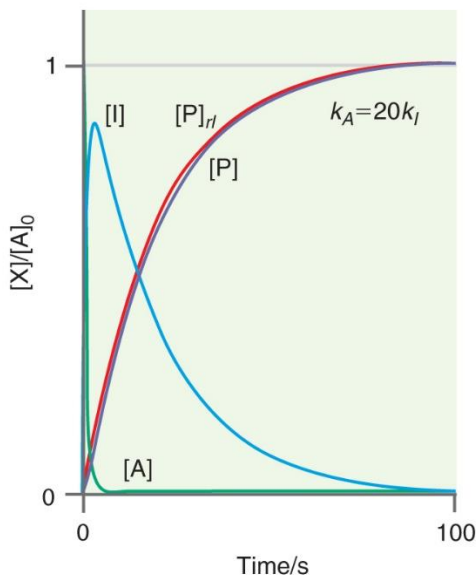
$$[P](t) = [A]_o \left(\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right) \rightarrow (1 - e^{-k_I t})[A]_0$$

so the production rate depend on the rate constant k_I. In other word the first step is fast and the second is slow, $A \overset{k_A}{\rightarrow} I \overset{k_I}{\rightarrow} P$. The slow step is called the rate limiting step. This is trivial in such a simple reaction but real reactions are often more complex.

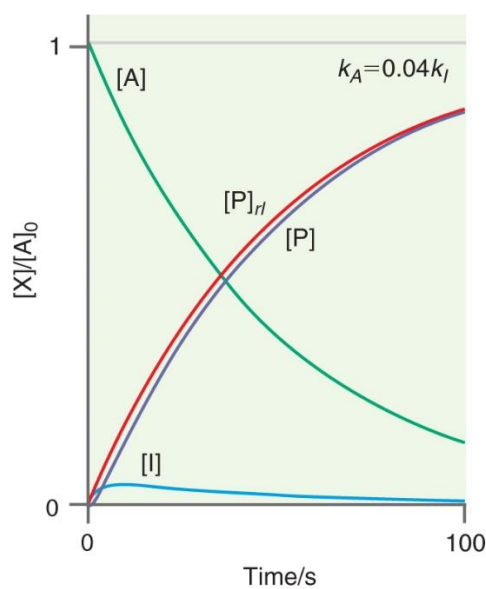The second limit is b) when $k_I \gg k_A$ and exp(-$k_I t$) << exp(-$k_A t$)

$$[P](t) = [A]_o \left(\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right) \rightarrow (1 - e^{-k_A t})[A]_0$$

in both cases the approximate equations describe the product behavior. In base b) it is easy to miss the intermediate state. Its concentration is very low.

(a)

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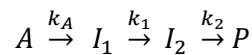
(b)

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The steady state approximation

In the case of sequential chemical reactions the reaction kinetics can in principle be solved from set of coupled differential equations. This will usually require numerical methods and this is not very convenient. There are some ways to approximate the rate equations. The most convenient approximation is the steady-state approximation. In this approximation the *intermediate* concentrations are assumed to be rather constant or

$$\frac{d[I_A]}{dt} = 0$$

Mathematically this would simplify the differential equations to ordinary equation and very complex reactions can be solved.

We can study a reaction path with two intermediate states

$$A \xrightarrow{k_A} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} P$$

in steady-state

$$\frac{d[I_1]}{dt} = k_A[A] - k_1[I_1] = 0,$$

$$[I_1] = \frac{k_A}{k_1}[A], \quad \frac{d[I_2]}{dt} = k_1[I_1] - k_2[I_2] = 0, \quad [I_2] = \frac{k_1}{k_2}[I_1] = \frac{k_A}{k_2}[A]$$
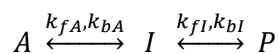
the product forming rate is

$$\frac{d[P]}{dt} = k_2[I_2] = k_A[A], \quad [A] = [A]_0 e^{-k_A t} \implies \frac{d[P]}{dt} = k_A[A]_0 e^{-k_A t}$$
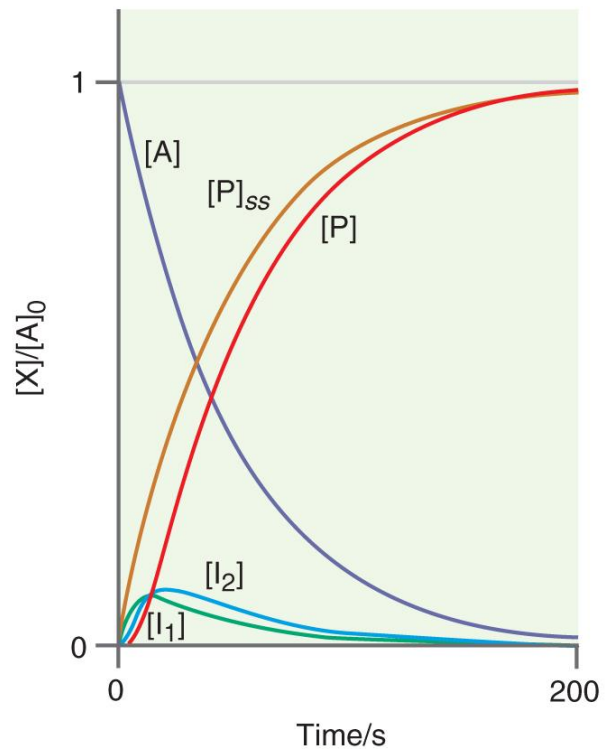
the last equation can be integrated

$$[P] = [A]_0(1 - e^{-k_A t})$$

The s-s approximation works well if the intermediate rate constant k_1 and k_2 are large compared to k_A (case b) above.

The steady-state approximation work also if the backward reactions are included

$$A \underset{k_{fA}, k_{bA}}{\xleftrightarrow{\hspace{1.5cm}}} I \underset{k_{fI}, k_{bI}}{\xleftrightarrow{\hspace{1.5cm}}} P$$

This will be discussed later in the book so we will come back to this later. Overall, the steady-state approximation is a very powerful tool to analyze complex reactions.
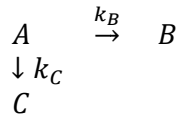
Parallel reactions   Engel & Reid chapter 35.8

Reactions can have several reaction channels

$$A \xrightarrow{k_B} B$$
$$\downarrow k_C$$
$$C$$

$$\frac{d[A]}{dt} = -k_B[A] - k_C[A], \quad \frac{d[B]}{dt} = k_B[A], \quad \frac{d[C]}{dt} = k_C[A]$$

$$[B] = \frac{k_B}{k_B + k_C}[A]_0\left(1 - e^{-(k_B+k_C)t}\right), \quad [C] = \frac{k_C}{k_B + k_C}[A]_0\left(1 - e^{-(k_B+k_C)t}\right)$$

so the concentrations of B and C depend on the reaction constants k_B and k_C

$$\frac{[B]}{[C]} = \frac{k_B}{k_C}$$

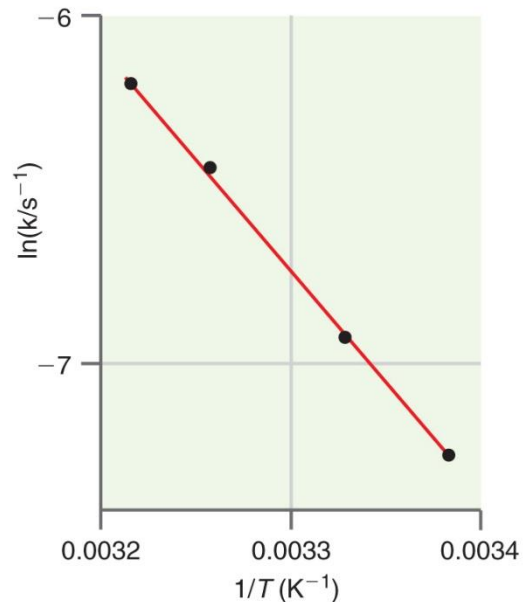# Temperature dependence of rate constant   Engel & Reid chapter 35.9

One of the key observation of reactions is the temperature dependence of rate constant. It is the famous Arrhenius law

$$k = Ae^{-E_a/RT}$$

here the E_a is the activation energy and A is a prefactor that contain the reaction entropy. It is clear that the reaction rates will increase rapidly with respect of temperature.

The parameters of Arrhenius law are easy to determine ln(k) vs 1/T plot. The slope is the activation energy and the interception give the prefactor.
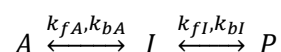
Examine the problem 35.8

Reversible reactions   Engel & Reid chapter 35.10

It is important to remember that every reaction will have forward and backward reaction constants

$$A \xleftrightarrow{k_{fA}, k_{bA}} I \xleftrightarrow{k_{fI}, k_{bI}} P$$

Earlier we studied a lot of the equilibrium. To have consistent kinetic model we need to include the backward reactions.

The kinetics of this reaction is:

$$\frac{d[A]}{dt} = -k_{fA}[A] + k_{bA}[I],$$

$$\frac{d[I]}{dt} = k_{fA}[A] - k_{bA}[I] - k_{fI}[I] + k_{bI}[P],$$

$$\frac{d[P]}{dt} = k_{fI}[I] - k_{bI}[P]$$

this is quite complex, so let us look a simpler reaction $A \xleftrightarrow{k_f, k_b} B$, the kinetics is

$$\frac{d[A]}{dt} = -k_f[A] + k_b[B], \quad \frac{d[B]}{dt} = k_f[A] - k_b[B]$$

Material is conserved $[A]_0 = [A] + [B]$ and the kinetic can be solved (detail are in the book)
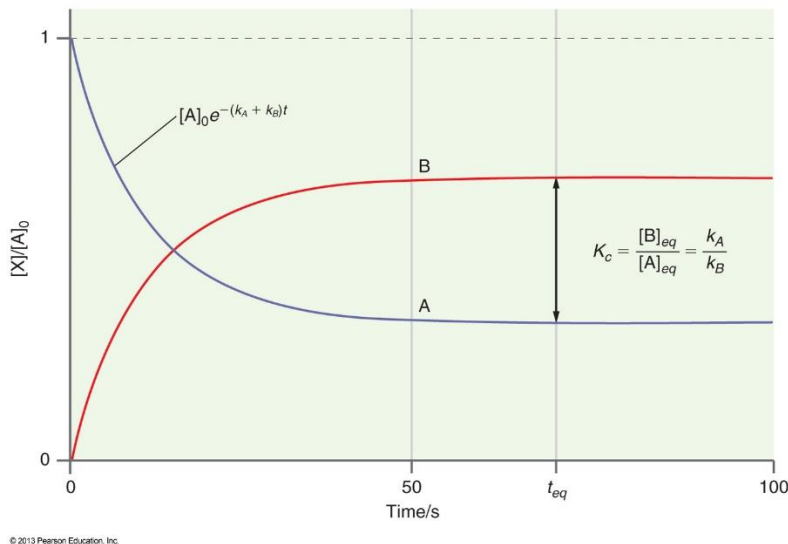
$$[A](t) = [A]_o \frac{k_f + k_b e^{-(k_f + k_b)t}}{k_f + k_b}, \quad [B](t) = [A]_0 - [A](t)$$

The equilibrium constant is K=[B]/[A] the

$$[A]_{eq} = [A]_o \frac{k_f}{k_f + k_b}, \quad [B]_{eq} = [A]_0 (1 - \frac{k_f}{k_f + k_b})$$

and now (easy to derive at d[A]/dt=0: $\frac{d[A]}{dt} = -k_f[A]_{eq} + k_b[B]_{eq} = 0 \implies k_f[A]_{eq} = k_b[B]_{eq}$

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f}{k_b}$$

For the more complex reaction. At equilibrium

$$\frac{d[A]}{dt} = -k_{fA}[A] + k_{bA}[I] = 0 \implies K_{AI} = \frac{[A]}{[I]} = \frac{k_{bA}}{k_{fA}}$$

$$\frac{d[I]}{dt} = k_{fA}[A] - k_{bA}[I] - k_{fI}[I] + k_{bI}[P] = 0,$$

$$\frac{d[P]}{dt} = k_{fI}[I] - k_{bI}[P] = 0 \implies K_{PI} = \frac{[P]}{[I]} = \frac{k_{fI}}{k_{bI}}$$

$$K_{PA} = \frac{[P]}{[A]} = \frac{[P]}{[I]}\frac{[I]}{[A]} = \frac{k_{fA}}{k_{bA}}\frac{k_{fI}}{k_{bI}}$$
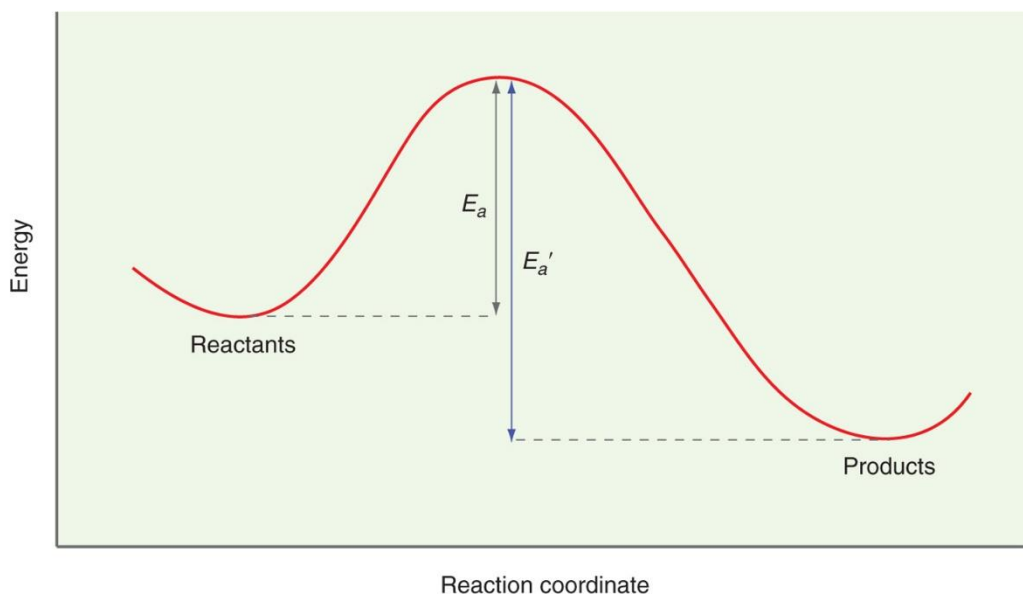
It is interesting that the PA equilibrium depend on the rate constants of the intermediate complex.

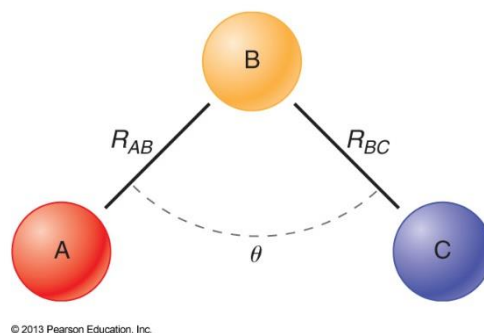| Reaction energy profile	Engel & Reid chapter 35.13

The reactions can be understood using a (free) energy profile. The reaction proceeds via a reaction coordinate. We discuss later the reaction coordinate and here we focus on the energy profile. The reaction free energy is the energy difference ΔG_r of reactants and products. (not in the figure). This will determine the equilibrium constant $K = \exp\left(-\frac{\Delta G_r}{RT}\right)$. The forward rate constant is determined by the energy barrier E_a, $k_f = A \exp\left(-\frac{E_a}{RT}\right)$ and the backward rate constant with barrier E'_a $k_b = A' \exp\left(-\frac{E'_a}{RT}\right)$. This is the Arrhenius Law. Here the activation energy instead the free energy is used, and this is a bit confusing. The activation energy is the internal energy and the entropy and PV term

are included to the prefactor A. A precise derivation of these equations uses the activated complex theory (chapter 35.14), which is outside of this course.
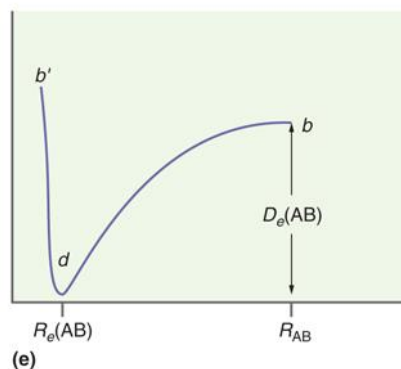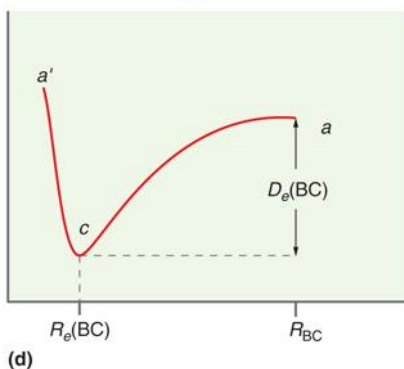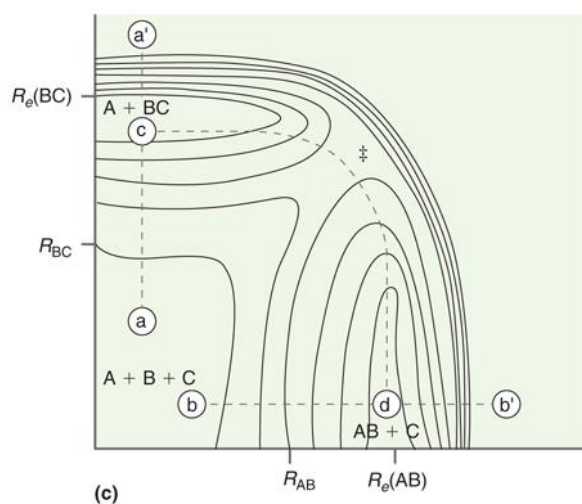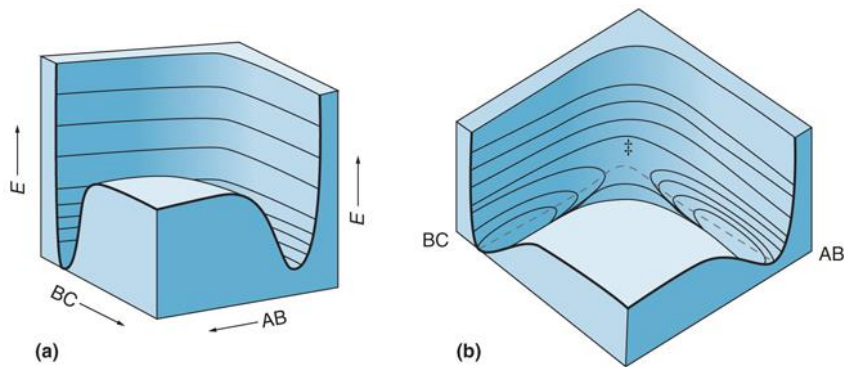
The reaction coordinate is quite "concrete". It describes the movement of all atoms in the reaction. On the right there is three atoms of reaction AB + C -> A + BC. In the beginning the distance AB is short (there is a chemical bond between them). The reaction proceeds, and at some point the bonds AB and BC are rather similar. At this point the reaction energy is at its maximum. This is the **transition state.** After it the energy will go down and the bond BC become short.

The total potential energy surface will describe the (free) energy at every atom position. This is very complex function. For 10 atoms it is 24 dimensional function, which is in practice impossible to measure. It can be computed using quantum chemical methods but only in few dimensions. See subfigure (c) below.

(a)

(b)

(c)

(d)

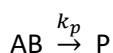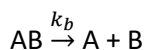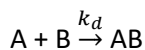(e)

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The reaction path is the lowest possible energy path from reactants to products. The transition state is the highest point in the reaction path and it position will determine the reaction rates.

Using the activated complex theory one can derive the precise equations and if you are interested of the details read the book.

Few remarks: in every reaction step there is a transition state. There can be different reaction paths between A and P and each of them have a transition state. If the reaction is endothermic the transition state is at least as high as the reaction energy.

If the transition state resembles the reactants is it called early transition state and if it resemble the products it called later TS.

Any reaction to happen the reactant molecules need to be very near (within a chemical bond distance) to each other. In gas phase this happen with molecular collision and in liquid via diffusion. Here we concentrate on the liquid phase. We note with AB the case where the molecules are near each other (this is not the transition state) and we can see the state AB as an intermediate state. Next the state AB can either broke (to A+B) or form the product P. The reaction steps are

A + B $\xrightarrow{k_d}$ AB

AB $\xrightarrow{k_b}$ A + B

AB $\xrightarrow{k_p}$ P

we can use the steady-state approximation

$\frac{d[AB]}{dt} = k_d[A][B] - k_b[AB] - k_p[AB] = 0$

and $[AB] = \frac{k_d}{k_b+k_p}[A][B]$ the reaction product

rate is $k_p[AB] = \frac{k_p k_d}{k_b+k_p}[A][B]$ if the rate constant $k_p \gg k_b$ (or most of the AB complexes will react further to product), the effective rate constant is k_d . In this case the diffusion will limit the reaction rate. This is called the **diffusion limited reaction**.

The other limit $k_b \gg k_p$ where most of the AB complexes broke back to A and B. Then the rate is
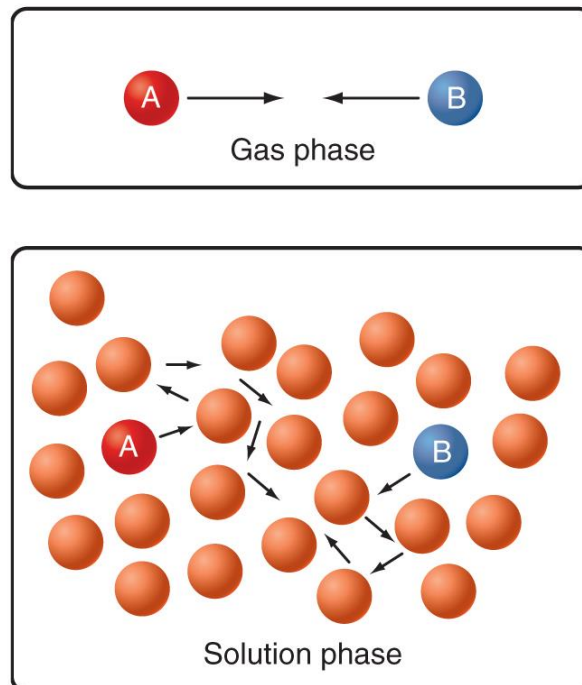
$\frac{k_p k_d}{k_b}[A][B]$.

The diffusion rate constant can be estimated as $k_d = 4\pi N_A(r_A + r_B)D_{AB}$ where D_{AB} is the intermolecular diffusion constant, $D_{AB} = D_A + D_B$ and r_A is the estimate of the radius of molecule A (or B).

For many molecules, the diffusion coefficient and rough estimation of their sizes are known.

See problem 35.11

The oxygen binding to hemoglobin has rate constant of $4*10^7$ 1/(Ms) (in water). What is the diffusion rate? The diffusion coefficients are $7.6*10^{-7}$ cm²/s (hemog) and $2.2*10^{-5}$ cm²/s (oxygen). The sizes (radius) are 35 Å (hemog) and 2 Å (oxygen). Is the reaction diffusion limited?

With these we can compute the k_d= $6.4*10^{10}$ 1/(Ms). This is much larger than the observed rate so the rate is limited by the reaction.

Note that the diffusion rate estimation is only estimation. So only, if the rates differ significantly conclusion can be made.
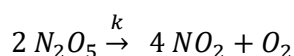

| Complex reactions | Engel & Reid chapter 36 |

There are several interesting reactions in this chapter especially the catalysis and photochemical reactions. We do not have time to go through all of this. But if you have time try to also read the end of the chapter.
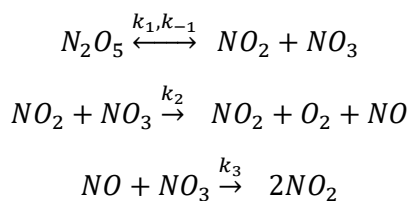
Intermediate reactions

We usually write the chemical reactions from reactants to products but there are often some intermediates. Those can be difficult to detect but there are several hints that they exist.

Let us look the following reaction

$$2 N_2O_5 \xrightarrow{k} 4 NO_2 + O_2$$

Its experimental rate law is linear to $[N_2O_5]$. In the reaction equation there are two N_2O_5 molecules and then the rate should be second order for $[N_2O_5]$.

There is a suggestion for intermediate reactions

$$N_2O_5 \xleftrightarrow{k_1,k_{-1}} NO_2 + NO_3$$

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

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

The rate of the reaction is

$$R = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}(k_1[N_2O_5] - k_{-1}[NO_2][NO_3])$$

now we need to look the intermediates and we will use the steady-state approximation

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \implies [NO] = \frac{k_2}{k_3}[NO_2]$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - (k_{-1} + k_2)[NO_2][NO_3] - k_3[NO][NO_3] = 0$$

$$\Rightarrow k_1[N_2O_5] - (k_{-1} + k_2)[NO_2][NO_3] - k_2[NO_2][NO_3] = 0$$

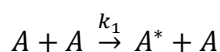$$k_1[N_2O_5] - (k_{-1} + 2k_2)[NO_2][NO_3] = 0 \implies [NO_2][NO_3] = k_1/(k_{-1} + 2k_2)[N_2O_5]$$

and the rate is
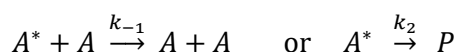
$$R = \frac{k_1 k_2}{k_{-1} + 2k_2}[N_2O_5]$$

The rate is of first order. The difficult part is to find the intermediate reactions.

Lindeman mechanism

Unimolecular reactions are usually assumed to be first order. In pure systems (only one component) this is not necessarily correct. Usually the reaction have some barrier and the molecule need energy to cross this barrier. The energy come from collision to another molecule. The activated molecule is denoted with *.

$$A + A \xrightarrow{k_1} A^* + A$$

The activation can end in a collision or the molecule can react.

$$A^* + A \xrightarrow{k_{-1}} A + A \quad \text{or} \quad A^* \xrightarrow{k_2} P$$

The reaction rate is $k_2[A^*]$ and using the steady-state approximation

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0 \implies [A^*]$$

$$= \frac{k_1[A]^2}{k_{-1}[A] + k_2}, \quad R = \frac{k_2 k_1[A]^2}{k_{-1}[A] + k_2}$$

This is not linear. If $k_{-1}[A] \gg k_2$ then $R = k_{\text{eff}}[A]$ so at high pressures concentrations of A the normal assumption is valid. At low pressures or $k_{-1}[A] \ll k_2$ then $R = k_1[A]^2$.

This same problem can be written to a mixed system, where the reacting molecule is A and there is some inert gas or liquid M.
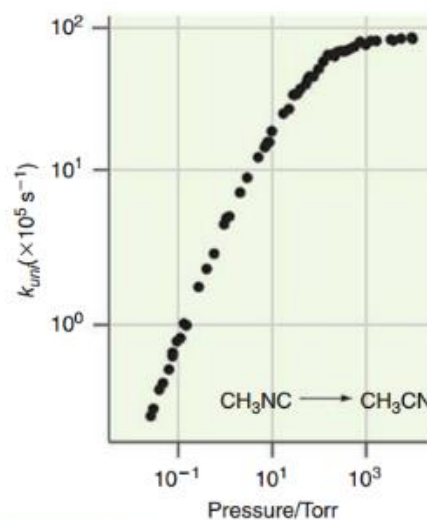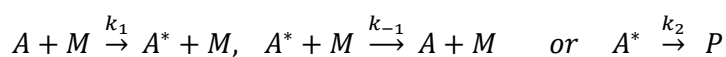
$$A + M \xrightarrow{k_1} A^* + M, \quad A^* + M \xrightarrow{k_{-1}} A + M \quad \text{or} \quad A^* \xrightarrow{k_2} P$$

FIGURE 36.1

Pressure dependence of the observed rate constant for the unimolecular isomerization of methyl isocyanide.
[Data from Schneider and Rabinovitch, "Thermal Unimolecular Isomerization of Methyl Isocyanide - Fall-Off Behavior," *J. American Chemical Society* 84 (1962): 4225.]

now

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0 \implies [A^*]$$

$$= \frac{k_1[A][M]}{k_{-1}[M] + k_2},$$

$$R = \frac{k_2 k_1[M]}{k_{-1}[M] + k_2}[A] = k_{eff}[A]$$

in this case the reaction is always linear with respect to A. The k_{eff} depend on concentration of M. One can write this equation as

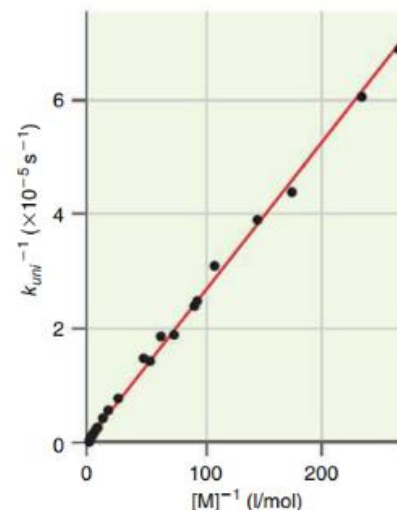$$\frac{1}{k_{eff}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1}\frac{1}{[M]}$$

FIGURE 36.2
Plot of k_{uni}^{-1} versus $[M]^{-1}$ for the unimolecular isomerization of methyl isocyanide at 230.4°C. The solid line is the best fit to the data.

| Catalysis | Engel & Reid chapter 36.4 |

Catalysis is one of the most important topics in chemistry. Often the reactions are slow but with some catalyst the reaction rate can be improved enormously. Chemical industry is using catalyst a

lot and most biochemical reactions are (protein) catalyzed. In catalysis the reacting molecules (or one of them) are bound to some catalyst. The reaction equation is very simple (S is the reacting molecule, C catalyst and P product). The catalyst is not consumed in the reaction.

$$S + C \xrightleftharpoons{k_1, k_{-1}} SC, \ SC \xrightarrow{k_2} P + C$$

We use the steady-state approximation

$$\frac{d[SC]}{dt} = k_1[S][C] - k_{-1}[SC] - k_2[SC] = 0 \ \Rightarrow \ [SC] = \frac{k_1}{k_{-1} + k_2}[S][C]$$

$$= [S][C]/K_m$$

the rate is

$$\frac{d[P]}{dt} = \frac{k_2}{K_m}[S][C] \ \text{ and } \ K_m = \frac{[S][C]}{[SC]} = \frac{k_{-1} + k_2}{k_1}$$

Enzyme (E)　　　Substrate (S)

Enzyme–substrate complex (ES)

Product (P)

FIGURE 36.6
Schematic of enzyme catalysis.

K_m is the equilibrium constant of [S][C] and [SC]. Typically, the k_2 is much larger than the rate constant of an uncatalyzed reaction. This is form is bit inconvenient since we do not know the [S] and [C] during the reaction but we can use the initial values $[S]_0 = [S] + [SC] + [P]$ and $[C]_0 = [S] + [SC]$. Next we assume that $[SC]^2$ and [P] are small. With these assumptions we get (see the steps from the book)

$$[SC] = \frac{[S]_o[C]_o}{[S]_o + [C]_o + K_m}$$

and the early state rate is (this assumes that [P] is small)

$$R_o = \frac{d[P]}{dt} = \frac{k_2[S]_o[C]_o}{[S]_o + [C]_o + K_m}$$

if $[S]_0 \gg [C]_0$ so there is much more reacting molecules than catalyst

$$R_o = \frac{k_2[S]_o[C]_o}{[S]_o + K_m}$$

and if $[C]_0 \gg [S]_0$

$$R_o = \frac{k_2[S]_o[C]_o}{[C]_o + K_m}$$

Michaelis-Menten reaction

MM reaction is a good example of catalysis or enzyme catalysis. The main reaction is the same as above

$$S + C \xrightleftharpoons{k_1, k_{-1}} SC, \ SC \xrightarrow{k_2} P + C$$

We can look this on the limit $[S]_0 \gg [C]_0$ and $[S]_0 \gg K_m$ this determinate the maximum rate $R_{max} = k_2[C]_o$ now we can rewrite the early state rate as (Lineweaver-Burk plot)
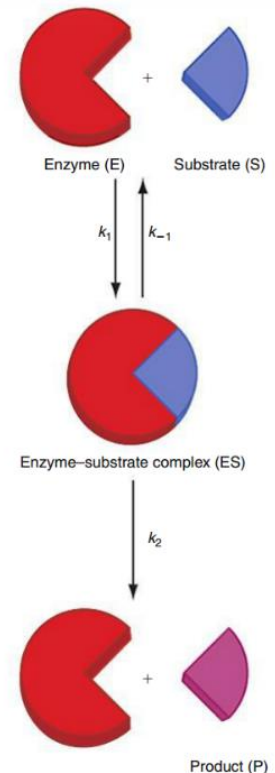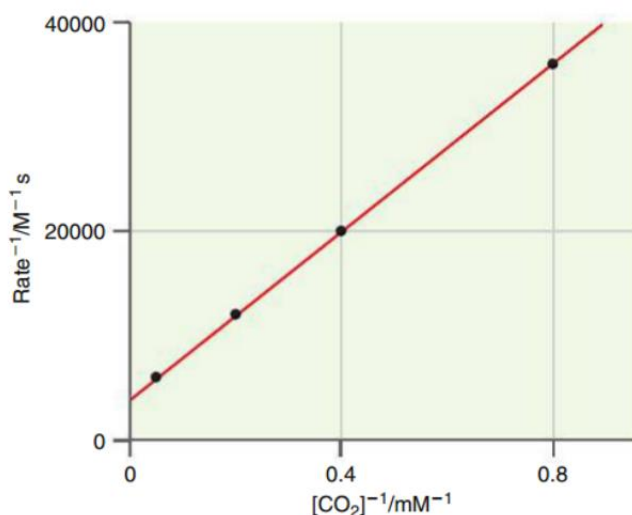
$$\frac{1}{R_o} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}\,[S]_o}$$

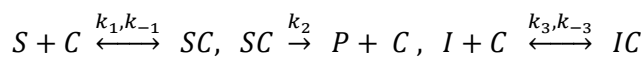with this we can easily determine the R_{max} and K_m

See Example 36.1.

The slope of the 1/R vs 1/[S]$_o$ plot is K_m/R_{max} and the interception is $1/R_{max}$

The Lineweaver–Burk plot of the rate^{-1} versus $[CO_2]^{-1}$ is shown here:

Competitive inhibition in catalysis or catalysis poisoning

Sometimes another molecule can bind to the catalyst. In biochemistry this is called competitive inhibition and catalysis research catalyst poisoning. We denote the inhibitor are I and when it is bound to catalyst the catalyst is inactive
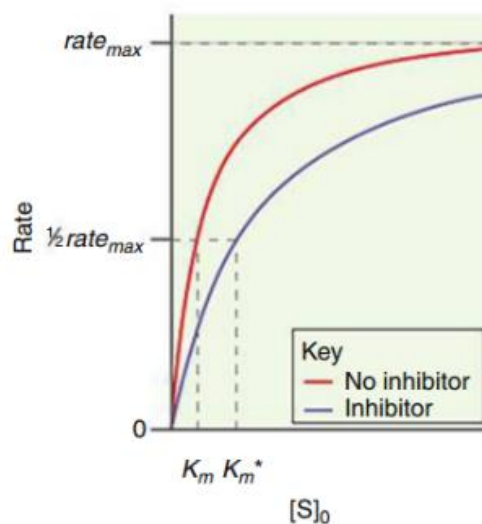
$$S + C \xrightarrow{k_1,k_{-1}} SC, \;\; SC \xrightarrow{k_2} P + C\,, \;\; I + C \xrightarrow{k_3,k_{-3}} IC$$

The total catalyst is

$$[C]_0 = [C] + [SC] + [IC]$$

and we have two equilibrium constants

$$K_s = \frac{[S][C]}{[SC]} \approx K_m, \qquad K_i = \frac{[I][C]}{[IC]}$$

With assumptions that k_2 is small the rate can be written

$$R = \frac{d[P]}{dt} = k_2[SC] = \frac{k_2[S][C]_o}{[S] + K_m(1 + \frac{[I]}{K_i})}$$

we can also assume that [EC] and [P] << [S] then

$$R_o = \frac{k_2[S]_o[C]_o}{[S]_o + K_m(1 + \frac{[I]}{K_i})}$$

These equations are similar to the ones above but the K_m is enhanced with the inhibition. We can shorten the using effective K_m, $K_m^* = K_m(1 + \frac{[I]}{K_i})$. Now the Lineweaver-Burk plot can be used to analyze the reaction.
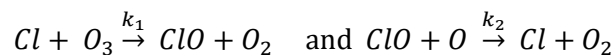
$$\frac{1}{R_o} = \frac{1}{R_{max}} + \frac{K_m^*}{R_{max}}\frac{1}{[S]_o}$$

If the inhibitor does not bind strongly to the catalyst or its concertation is low (<< K_i) it does not harm the reaction much but this is not always the case. Pt is commonly used catalyst in chemical industry and it is sensitive for lead (Pb) and sulphur (S) poisoning. That's why you cannot use lead or high S containing fuel in car that have catalysator. Lead is very strong catalyst poison and it will destroy Pt catalyst almost forever. In biochemistry some drugs act as a catalyst poison. The drug can slow or stop some biochemical catalyst and for example kill bacteria.
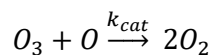

Homogenous and heterogenous catalysis

In chemical catalyst the catalyst is divided to homogenous and heterogenous catalysis. In homogenous catalyst the catalyst is in the save phase as the reactants.

An example, Rowland and Molina proposed that Cl atom will catalytically destroy ozone (O_3) in stratosphere and causing the ozone hole. The main reaction is simple
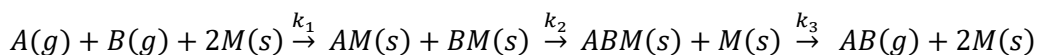
$$Cl + O_3 \xrightarrow{k_1} ClO + O_2 \quad \text{and} \quad ClO + O \xrightarrow{k_2} Cl + O_2$$

the net reaction is

$$O_3 + O \xrightarrow{k_{cat}} 2O_2$$

Here the Cl is the catalyst and it is gas phase. The same reaction can happen without the catalyst but the catalysed reaction is ca. 74 times faster and a single Cl atom can broke thousands ozone molecules. In stratosphere the main source of Cl is chlorofluorocarbons (CFC's), like $CFCl_2$.

Surface catalysis is the main type of **heterogenous catalyst**. There the reacting molecules (A and B) will bind to a surface like Pt (M) and react on it.

$$A(g) + B(g) + 2M(s) \overset{k_1}{\rightarrow} AM(s) + BM(s) \overset{k_2}{\rightarrow} ABM(s) + M(s) \overset{k_3}{\rightarrow} AB(g) + 2M(s)$$

The adsorption of the molecule A can modelled with the Langmuir isotherm

$$\theta_A = \frac{KP_A}{KP_A + 1}$$

where θ_A is the coverage of molecule A ($\theta_A = 1$ means that the whole surface is covered with A.) and K is the binding constant of A, P_A is the partial pressure of A.

If there are two gases the Langmuir isotherms are

$$\theta_A = \frac{K_A P_A}{K_A P_A + K_B P_B + 1}, \quad \theta_B = \frac{K_B P_B}{K_A P_A + K_B P_B + 1}$$
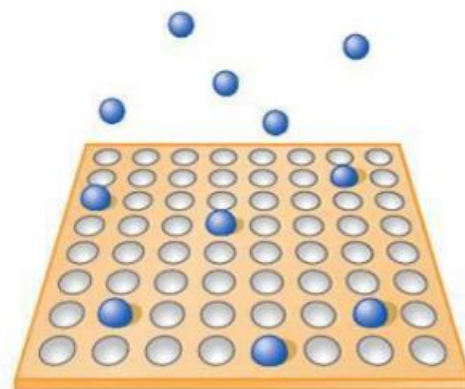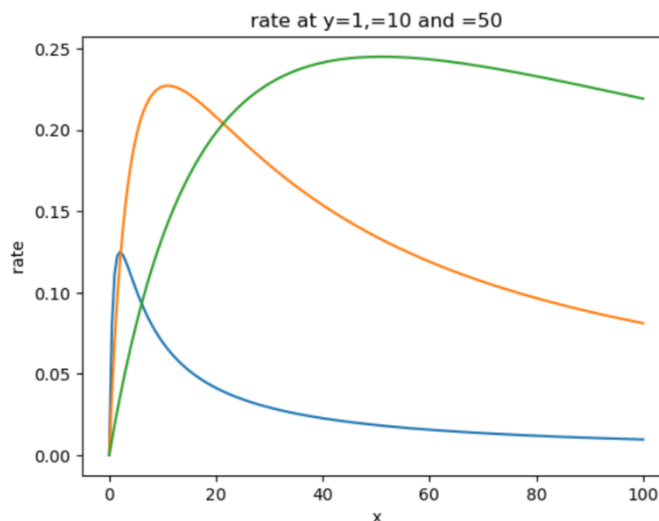

FIGURE 36.10

If the step 2 (AM + BM -> ABM) is the rate limiting step (which it usually is) the rate of the total reaction is

$$R = k_2 \theta_B \theta_A = \frac{k_2 K_A P_A K_B P_B}{(K_A P_A + K_B P_B + 1)^2} = \frac{k_2 xy}{(x + y + 1)^2}$$

The maximum rate is achieved when x=y or the surface coverage is equal. For example, if $K_A = 10K_B$ the optimal partial pressure ratio is 1/10. This equation give a very simple tool to control the reaction.

The rest of chapter 36

There are a lot of interesting topics in the end of this chapter. They are not included to the course but some of them are useful. Like chain reaction and photochemistry.