Ch. 28 → Chemical Kinetics ; Rate Laws.

For the reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_Y Y + \nu_Z Z$

we define the rate of reaction $v(t)$ as (forward rate)

$$v(t) = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_Y}\frac{d[Y]}{dt} = \frac{1}{\nu_Z}\frac{d[Z]}{dt}$$

ex $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

$$v(t) = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

The relationship between $v(t)$ and the concentrations is called the rate law.

Sometimes it is given by the stoichiometry, e.g. $v(t) = k[NO]^2[O_2]$ but this is not common.

The rate law comes from analyzing the mechanism (sequence of elementary steps) and not from the stoichiometry. Ch. 29

It is possible to have fractional powers, e.g. $Cl_2(g) + CO(g) \rightleftharpoons Cl_2CO(g)$ $v(t) = k[Cl_2]^{3/2}[CO]$

in which case we say the reaction is 3/2 order in Cl_2 and first order in CO, giving a forward rate law of order 5/2.

The rate law can be even more complicated in which case the concept of reaction order is not meaningful.

e.g. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

$$v(t) = \frac{k'[H_2][Br_2]^{1/2}}{1 + k''[HBr][Br_2]^{-1}}$$

Rate Laws must be determined experimentally, such as with the method of initial rates.

First order reactions 28-3 :

$$A + B \rightleftharpoons \text{products}$$

Suppose the rate law is first order in A. Then

$$v(t) = -\frac{d[A]}{dt} = k[A] \Longrightarrow \frac{d[A]}{[A]} = -k\,dt$$

Integrate: $\displaystyle\int_{[A]_0}^{[A]} \frac{1}{[A]}\,d[A] = -k\int_0^t dt \Rightarrow \ln\frac{[A]}{[A]_0} = -kt$

$\Longrightarrow \ln[A] = \ln[A]_0 - kt$ so a plot of $\ln[A]$ versus t would give a straight line with slope $-k$; intercept $\ln[A]_0$.

e.g. $N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2}O_2(g)$ is first order.

$$v(t) = -\frac{d[N_2O_5]}{dt} = k[N_2O_5].$$

$t_{1/2}$ = half-life = time required for half of the reactant to disappear.

From $\ln \frac{[A]}{[A]_0} = -kt$ we get, for $t = t_{1/2} \Rightarrow [A] = [A]_0/2$;

$$\ln 1/2 = -kt_{1/2} \Longrightarrow t_{1/2} = \frac{\ln 2}{k}$$

Independent of $[A]_0 \Rightarrow$ time it takes for "the next half" to disappear is constant.

Second order: suppose the rate law is $-\frac{d[A]}{dt} = k[A]^2$ for $A + B \rightleftharpoons$ products

$$\Longrightarrow \frac{d[A]}{[A]^2} = -k\,dt \quad \text{Integrate} \int_{[A]_0}^{[A]} \frac{1}{[A]^2}\, d[A] = -k\int_0^t dt$$

$$\Longrightarrow -\frac{1}{[A]} + \frac{1}{[A]_0} = -kt \Longrightarrow \frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

so a plot of $\frac{1}{[A]}$ vs t gives a straight line with slope k, intercept $\frac{1}{[A]_0}$.

half-life: put $t = t_{1/2}$ and $[A] = [A]_0/2$ to get

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt_{1/2} \Longrightarrow 2 = 1 + [A]_0 k t_{1/2} \Longrightarrow t_{1/2} = \frac{1}{k[A]_0}$$

depends on $[A]_0$.

What about second order kinetics where the reaction is first order in both [A] and [B]?

$$A + B \rightleftharpoons \text{products}$$

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

See Eq. 28.32 and 28.33 in textbook

Zeroth order: $A \rightarrow$ products, rate $= k[A]^0 = k$

$$-\frac{d[A]}{dt} = k \Rightarrow d[A] = -k\,dt$$ e.g. $2NH_3(g) \rightarrow 3H_2(g) + N_2(g)$

Integrate: $\int_{[A]_0}^{[A]} d[A] = -k\int_0^t dt \Rightarrow [A] = [A]_0 - kt$

so a plot of [A] vs t gives a straight line with slope $-k$ and intercept $[A]_0$.

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§28.5: reactions don't always go to completion

We write $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ with forwards and backwards rates k_1, k_{-1}.

At equilibrium we know that

$\frac{[B]_{eq}}{[A]_{eq}} = K_c$ where K_c is the equilibrium constant in terms of concentrations.

We also have $-\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$ no net reaction at equil.

If the reaction is first order in both [A] and [B]

we have $-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$ because

$k_1[A]$ depletes A while $k_{-1}[B]$ replenishes A.

If $[A] = [A]_0$ and $[B] = \cancel{[B]_0}^{\,0}$ at $t = 0$, $[B] = [A]_0 - [A]$

and $-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B] = (k_1 + k_{-1})[A] - k_{-1}[A]_0$

which integrates to (see problem 28-32)

$$[A] = ([A]_0 - [A]_{eq})e^{-(k_1+k_{-1})t} + [A]_{eq}$$

rearranging gives $\ln([A] - [A]_{eq}) = \ln([A]_0 - [A]_{eq}) - (k_1 + k_{-1})t$

so that a plot of $\ln([A] - [A]_{eq})$ vs t has slope $-(k_1 + k_{-1})$

and intercept $\ln([A]_0 - [A]_{eq})$.

This lets us determine $(k_1 + k_{-1})$ experimentally.

Also, at equil., $\frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}} = K_c$

So if we know $(k_1 + k_{-1})$ and we know K,

both the forwards and backwards rate constants

k_1 and k_{-1} can be determined.

§28-6. Temperature-jump experiments

method for studying fast reactions

Idea: take a system out of equilibrium by suddenly (instantaneously) changing the temperature, and then monitor what happens as the system comes to equilibrium under the new conditions.

Recall that $\Delta G^\circ_{rxn} = -RT \ln K \Rightarrow K = e^{-\Delta G^\circ_{rxn}/RT}$

Thus a small change in T can cause a large change in the equilibrium concentrations.

Consider $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ and assume simple, first order kinetics, namely $\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$

Recall that $\ln\left(\frac{K(T_2)}{K(T_1)}\right) = -\frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ section 26-7

and assume $\Delta H^\circ_{rxn} < 0$ for concreteness

Write $[A] = [A]_{2,eq} + \Delta[A]$

$[B] = [B]_{2,eq} + \Delta[B]$

since we know $[A]$ will come to $[A]_{2,eq}$ at T_2, but $[A] = [A]_{1,eq}$ at equil. under T_1, and we have just boosted the temperature to T_2.

Sub into $\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$ to get,

using that $[A]_{2,eq}$ and $[B]_{2,eq}$ are constants,

$$\frac{d\,\Delta[B]}{dt} = k_1[A]_{2,eq} + k_1\Delta[A] - k_{-1}[B]_{2,eq} - k_{-1}\Delta[B]$$

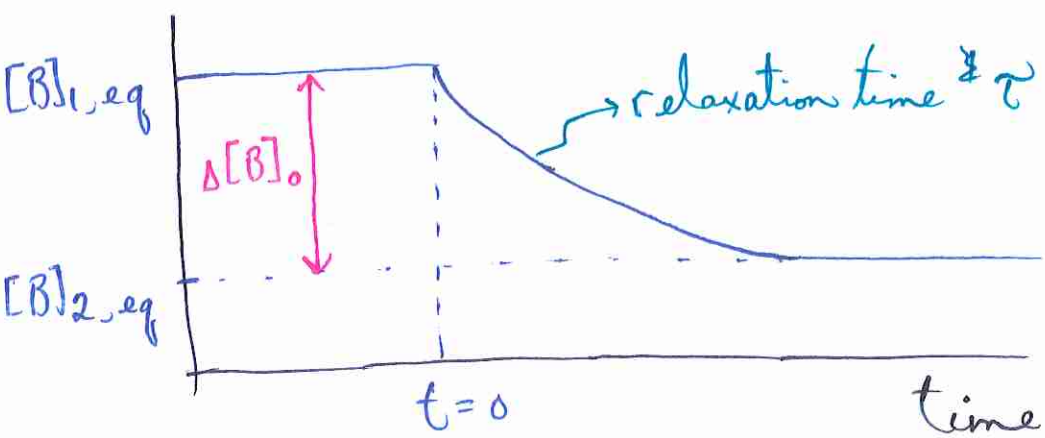
From the stoichiometry $\Delta([A]+[B]) = 0$

Also, the equil. conc. satisfy $k_1[A]_{2,eq} = k_{-1}[B]_{2,eq}$ (no net reaction)

giving $\frac{d\,\Delta[B]}{dt} = -(k_1 + k_{-1})\Delta[B]$

Easy to solve. Initial condition: $\Delta[B]_0$ at $t=0$ is $[B]_{1,eq} - [B]_{2,eq}$

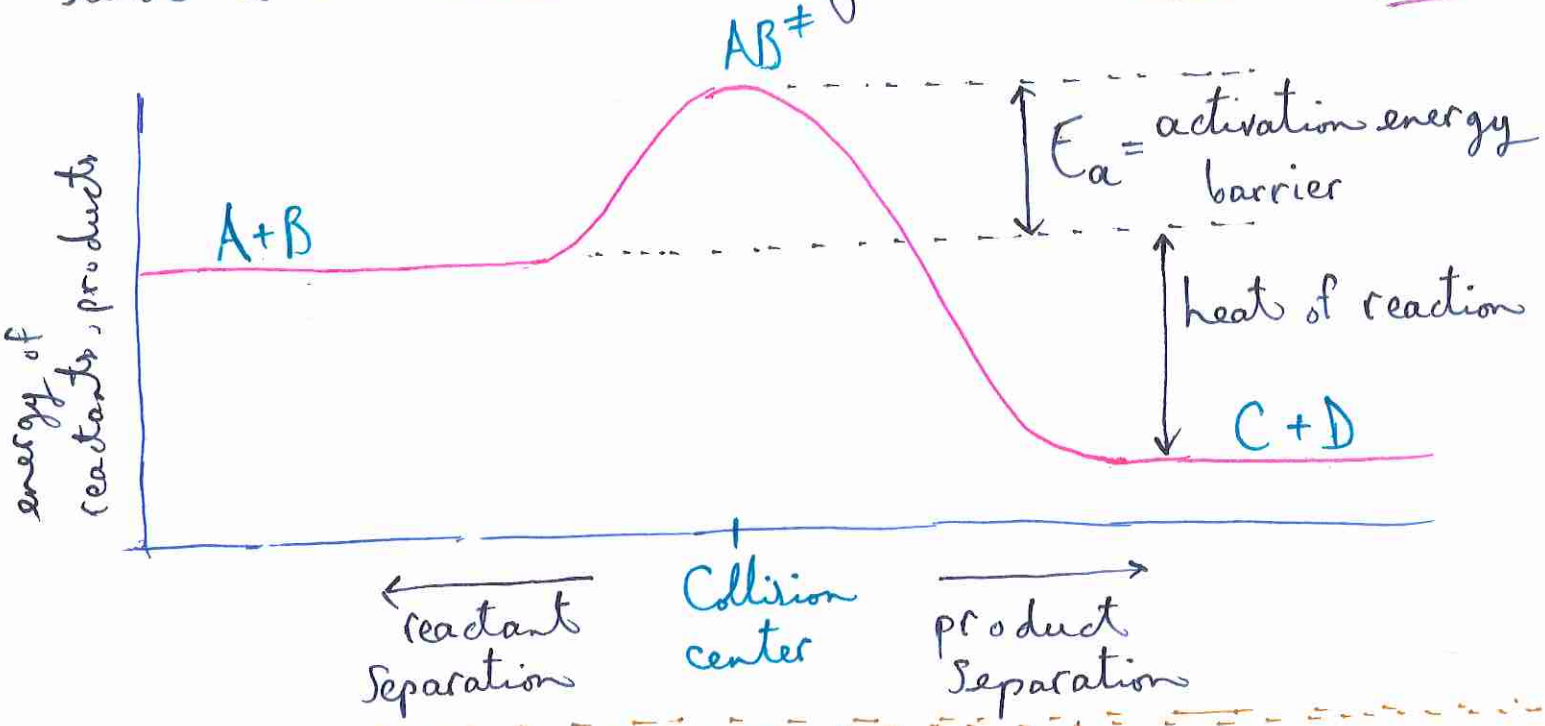
Solution: $\Delta[B] = \Delta[B]_0 e^{-t/\tau}$ with $\tau = \frac{1}{k_1 + k_{-1}}$



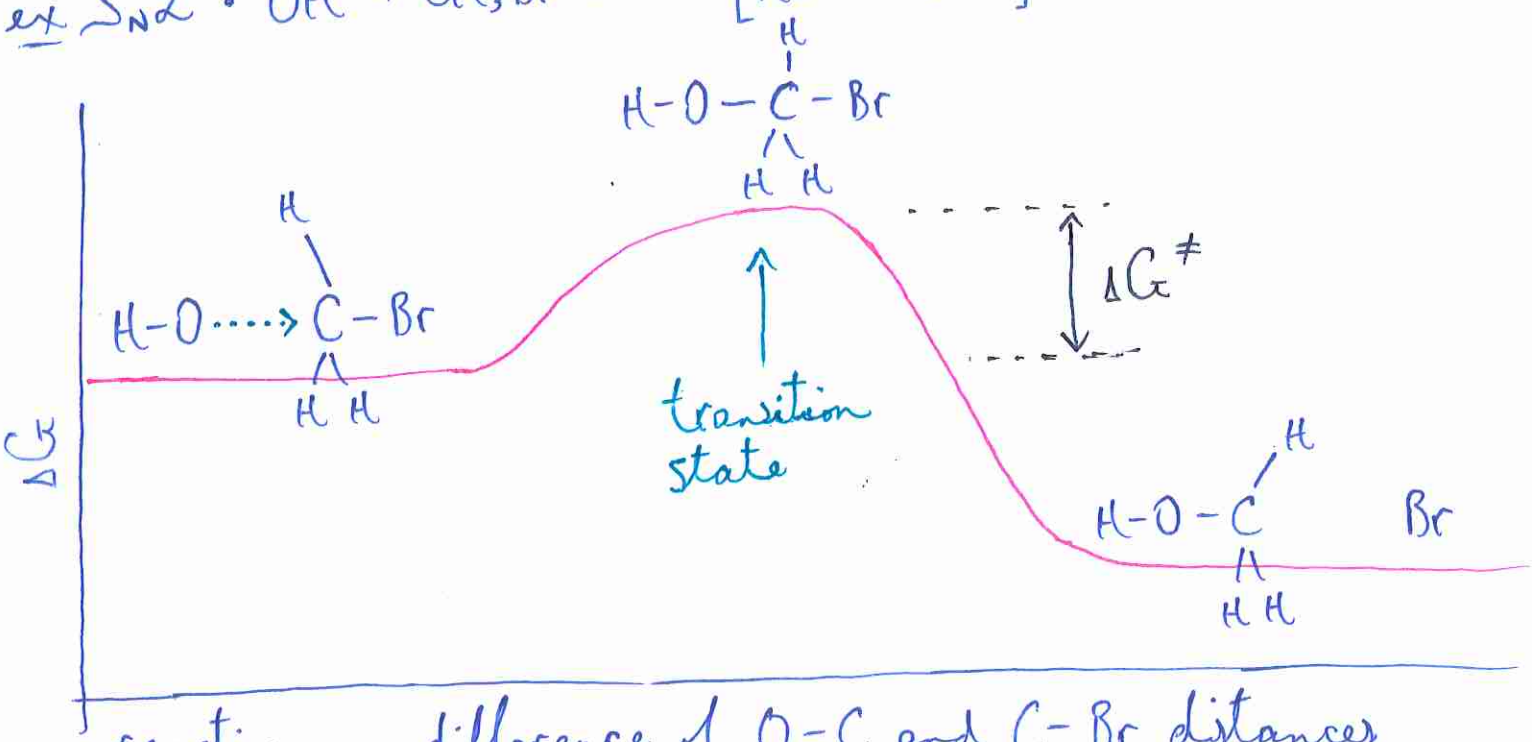
Can measure very fast rate constants in this way,

for example acid-base reactions in water, see Table 28.7

Before a chemical reaction can take place the molecules involved must be raised to a state of higher potential energy. They are then said to be activated or to form an activated complex.



ex S_N2 : $OH^- + CH_3Br \rightleftharpoons [HO-CH_3-Br]^{\neq} \longrightarrow CH_3OH + Br^-$



reaction coordinate = difference of O-C and C-Br distances
= d(O-C) - d(C-Br)

In 1889 Arrhenius said

① van't Hoff equation (26.29 in textbook) for the temperature dependence of the equilibrium constant is

$$\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2}$$

② law of mass action relates the equilibrium constant to the ratio of the forwards and backwards rate constants

$$K_c = k_f / k_b$$

Thus a reasonable equation for the variation of the rate constant with temperature is

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

E_a = activation energy

If E_a does not depend on T we can integrate:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

where $\ln A$ is the constant of integration

$$\Rightarrow k = A e^{-E_a/RT}$$

Arrhenius Equation

Interpretation: molecules must acquire a critical energy E_a before they can react. $e^{-E_a/RT}$ is the fraction of molecules that obtain the necessary energy.

Transition State Theory:

Henry Eyring said: the rate of reaction is the number of activated complexes passing per second over the top of the potential energy barrier.

This rate is equal to the concentration of activated complexes times the average velocity with which a complex moves across to the product side.

$$A + B \rightleftharpoons [AB]^{\neq} \longrightarrow \text{products}$$

↳ assume equil. is established (steady state)

The equilibrium constant for the formation of the complex is $K^{\neq} = \dfrac{[AB]^{\neq}}{[A][B]}$

The rate of reaction is $-\dfrac{d[A]}{dt} = [AB]^{\neq} \times \left(\begin{array}{c}\text{rate of passage}\\ \text{over the barrier}\end{array}\right)$

The rate of passage over the barrier is equal to the frequency with which the complex flies apart into the products.

The activated complex flies apart when one of its vibrations becomes a translation, and what was formerly one of the bonds holding the complex together becomes simply the line of centers between separating fragments.

The frequency $\nu = \varepsilon/h$ where ε is the average energy of the vibration leading to breakup. ($\varepsilon = h\nu$ is also the energy of a photon)

We assume $\varepsilon = k_B T$ ($\frac{1}{2} k_B T$ is equipartition) to yield $\nu = k_B T/h$

The reaction rate is thus (assume 2nd order)

$$-\frac{d[A]}{dt} = k_2[A][B] = K^{\ddagger}[A][B]\, k_B T/h$$

with rate constant $k_2 = \frac{k_B T}{h} K^{\ddagger}$

$\Delta G^{\circ\ddagger} = -RT \ln K^{\ddagger}$ is the difference between the free energy of the activated complex and the reactants, in their standard states.

$$k_2 = \frac{k_B T}{h} e^{-\Delta G^{\circ\ddagger}/RT} = \underbrace{\frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}/R}}_{A} e^{-\Delta H^{\circ\ddagger}/RT}$$

$\hookrightarrow \approx E_a$ except for PV term which is negligible for condensed phase reactions

$\Delta G^{\circ\ddagger}, \Delta S^{\circ\ddagger}, \Delta H^{\circ\ddagger}$ are the free energy, the entropy, and the enthalpy of activation.

$\Delta S^{\circ\ddagger} < 0$ means the activated complex is more ordered than the reactants

> 0 means the entropy of the complex is greater than the entropy of the reactants

A loosely bound complex has a higher entropy of activation than a tightly bound one.

ex: $CH_3 + D_2 \longrightarrow CH_3D + D$

$\Delta S^{\circ\ddagger} = -83.5\ JK^{-1}mol^{-1}$

$< 0 \Rightarrow$ activated complex is more restricted than the reactants.

Also, see BBA 1511 (2001) 42-48
"Application of the transition state theory to water transport across cell membranes".