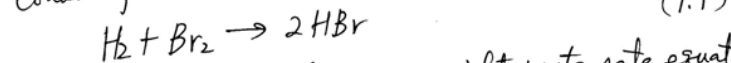# I. Kinetics of Complex reactions

I-1. Chain reactions

Rate law and reaction mechanism

Consider a reaction $\qquad$ (1.1)

$$H_2 + Br_2 \rightarrow 2HBr$$

According to the rate law, one might write rate equation as

$$-\frac{d[H_2]}{dt} = -\frac{d[Br_2]}{dt} = \frac{1}{2}\frac{d[HBr]}{dt} = k[H_2][Br_2] \qquad (1.2)$$

(i.e., following the stoichiometry of the reaction)

But, experimentally one finds that

$$\frac{1}{2}\frac{d[HBr]}{dt} = k[H_2][Br_2]^{\frac{1}{2}} \qquad (1.3)$$

which is different from (1.2) ! Why ?

The reason is that the <u>macroscopic</u> rate law is the consequence of reaction mechanism consisting of many elementary steps (or processes), each of which describes a process that takes place on the <u>microscopic</u> level.

Three types of microscopic processes account for essentially all reaction mechanisms
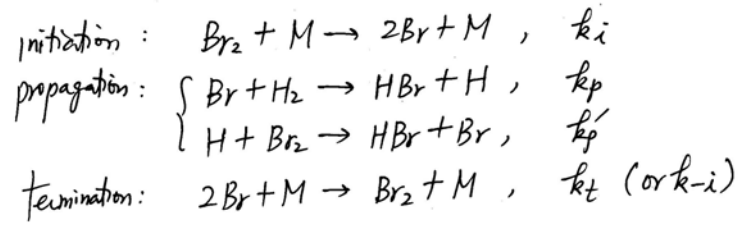
unimolecular reaction $\rightarrow$ first-order kinetics

bimolecular reaction $\rightarrow$ second-order kinetics

termolecular reaction $\rightarrow$ third-order kinetics

So, only for elementary chemical reaction (NOT necessarily for macroscopic overall reaction) the order of the reaction is equal to the molecularity.

Further investigations indicated that reaction (1.1) is in fact a chain reaction.

Initiation: $Br_2 + M \rightarrow 2Br + M$, k_i

propagation: $\begin{cases} Br + H_2 \rightarrow HBr + H, & k_p \\ H + Br_2 \rightarrow HBr + Br, & k_p' \end{cases}$

termination: $2Br + M \rightarrow Br_2 + M$, k_t (or k_{-i})

rate equations:

$$\frac{d[HBr]}{dt} = k_p[Br][H_2] + k_p'[H][Br_2]$$

$$\frac{d[Br]}{dt} = 2k_i[Br_2][M] - 2k_{-i}[Br]^2[M] - k_p[Br][H_2] + k_p'[H][Br_2]$$

$$\frac{d[H]}{dt} = k_p[Br][H_2] - k_p'[H][Br_2]$$

applying steady-state approximation to $[Br]$ and $[H]$

i.e. $d[Br]/dt = 0$ and $d[H]/dt = 0$

$$\therefore [Br] = \left(\frac{k_i}{k_{-i}}\right)^{1/2}[Br_2]^{1/2} \quad (why?) \quad (1.4)$$

and $\quad \dfrac{d[HBr]}{dt} = 2k_p[Br][H_2] \quad (why?)$

$$= 2k_p\left(\frac{k_i}{k_{-i}}\right)^{1/2}[H_2][Br_2]^{1/2} \quad (1.5)$$

So, the overall rate constant, $2k_p\left(\frac{k_i}{k_{-i}}\right)^{1/2}$, actually consists of three rate constants of elementary steps.

Homework 1

BUT, Atkin's book shows that the rate law follows

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{[Br_2] + k'[HBr]} \quad (1.6)$$

which is different from (1.5)!

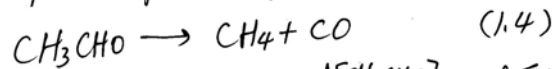why? which one is "correct"?

[Example 2] Prolysis of acetaldehyde (CH_3CHO)
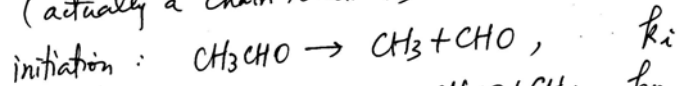
$$CH_3CHO \longrightarrow CH_4 + CO \qquad (1.4)$$

observed rate law : $-\dfrac{d[CH_3CHO]}{dt} = k\,[CH_3CHO]^{3/2}$ (1.5)

power of "$3/2$" (not "1") implies a complex reaction mechanism
(actually a chain reaction)

initiation : $CH_3CHO \longrightarrow CH_3 + CHO$, k_i

propagation : $\begin{cases} CH_3 + CH_3CHO \longrightarrow CH_3CO + CH_4, & k_p \\ CH_3CO \longrightarrow CH_3 + CO & , & k_p' \end{cases}$

termination : $CH_3 + CH_3 \longrightarrow C_2H_6$, k_t
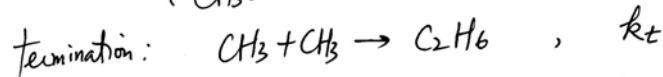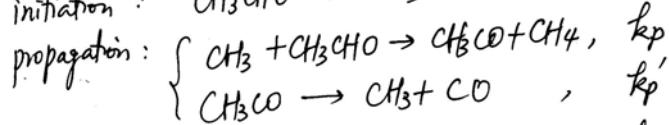
Applying steady state approximation to $[CH_3]$ and $[CH_3CO]$

$$\dfrac{d[CH_3]}{dt} = k_i[CH_3CHO] - k_p[CH_3][CH_3CHO] + k_p'[CH_3CHO] - 2k_t[CH_3]^2$$
$$= 0$$

$$\dfrac{d[CH_3CO]}{dt} = k_p[CH_3][CH_3CHO] - k_p'[CH_3CHO] = 0$$

$$\therefore \; [CH_3] = \left(\dfrac{k_i}{2k_t}\right)^{1/2} [CH_3CHO]^{1/2}$$

rate of formation of CH_4 is

$$\dfrac{d[CH_4]}{dt} = k_p[CH_3][CH_3CHO] = k_p\left(\dfrac{k_i}{2k_t}\right)^{1/2}[CH_3CHO]^{3/2} \quad (1.6)$$

which agrees with (1.5)

Again, the reaction (1.4) can be more complicated because other known by-products (CH_3COCH_3 , CH_3CH_2CHO etc) are not accounted for in the above reaction mechanism.

$\Rightarrow$ Often, there is no unique mechanism for a complex reaction.

I-2. Homogeneous catalysis

A catalysis is a substance that accelerates a reaction but undergoes no net chemical change. It lowers the activation energy of the reaction by providing an alternative path that avoids the slow, rate-determining step of the uncatalysed reaction.

[example]

$$2 H_2O_2(aq) \rightarrow 2 H_2O(l) + O_2(g)$$
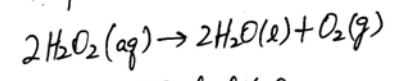
$Ea \simeq 18$ kcal/mol

if adding a little I^+

$Ea' \simeq 13.6$ kcal/mol

reaction rate increases 2000-fold.

if adding an enzyme
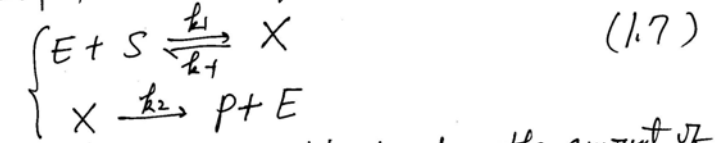
$Ea' \simeq 1.9$ kcal/mol !

rate increases by 10^{15} at 298K !!
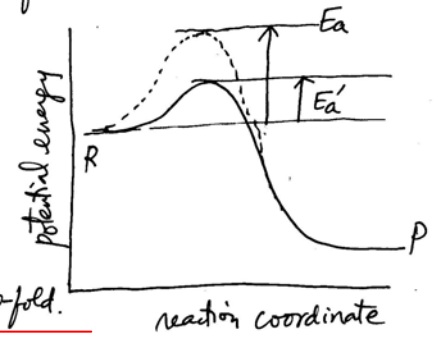
This is energetic considerations.

Kinetically, we will use the Michaelis-Menten mechanism for illustration.

Considering the reaction sequence

$$\begin{cases} E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \\ X \xrightarrow{k_2} P + E \end{cases} \qquad (1.7)$$

how does the rate of reaction depend on the amount of substrate [S] and the amount of enzyme [E] ?

steady state approximation to the intermediate [X]

$$\frac{d[X]}{dt} = k_1[E][S] - k_{-1}[X] - k_2[X] = 0 \qquad (1.8)$$

Let the original concentration of enzyme be E_0, and of substract be S_0. Then by mass balance

$$E_0 = [E] + [X]$$
$$S_0 = [S] + [X] + [P]$$

Substituting these into (1.8)

$$\frac{d[X]}{dt} = k_1 (E_0 - [X])(S_0 - [X] - [P]) - k_{-1}[X] - k_2[X] = 0 \quad (1.9)$$

In general $E_0 \ll S_0$; since $[X]$ can never be larger than E_0, if follows that $[X] \ll S_0$. If we now consider the initial rate of the reaction $d[P]/dt\big|_{t\to 0}$, where $[P] \approx 0$,

(1.9) can then be reduced to

$$[X] = \frac{k_1 E_0 S_0}{k_1 S_0 + k_{-1} + k_2} \quad (1.10)$$

$$\therefore \quad \frac{d[P]}{dt}\bigg|_{t\to 0} = k_2[X] = \frac{k_1 k_2 E_0}{k_1 + (k_{-1} + k_2)/S_0}$$

$$= \frac{V_m}{1 + K_m/S_0} \quad (1.11)$$

where $V_m = k_2 E_0$

$K_m = (k_{-1} + k_2)/k_1 \equiv$ Michaelis constant $= \dfrac{[E][S]}{[X]}$

At very high initial substrate concentrations,
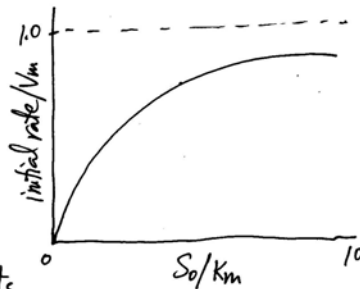
$$\frac{d[P]}{dt}\bigg|_{t\to 0} \simeq V_m = k_2 E_0$$

So, k_2 is also called the turnover number, which is the number of molecules of product per molecule of enzyme that can be created per unit time.

(1.11) can be rewritten as

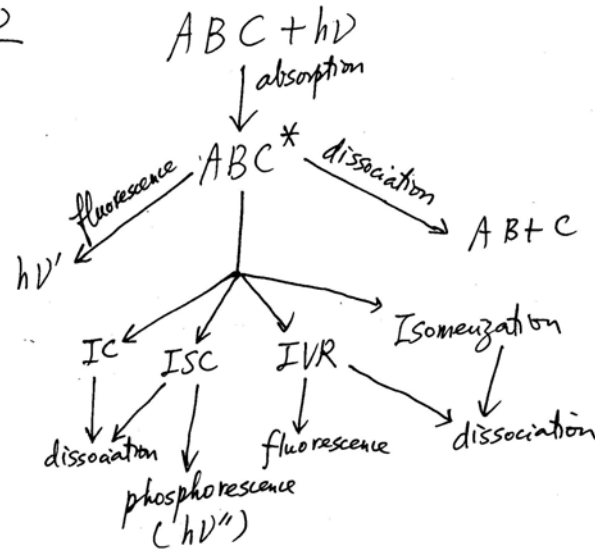$$\frac{1}{V_0} = \frac{1}{V_m} + \frac{K_m}{V_m S_0}$$

$$V_0 \equiv d[P]/dt\big|_{t\to 0}$$

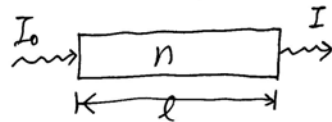a plot of $\frac{1}{V_0}$ vs. $\frac{1}{S_0}$ for determining the rate constants.

II. Photochemistry

Overview

$$ABC + h\nu$$

$\downarrow$ absorption

ABC^*

fluorescence $\swarrow$ $\qquad$ $\searrow$ dissociation

$h\nu'$ $\qquad\qquad\qquad$ $AB + C$

$\downarrow$

IC $\quad$ ISC $\quad$ IVR $\qquad$ Isomerization

dissociation $\qquad$ fluorescence $\qquad$ dissociation

phosphorescence

$(h\nu'')$
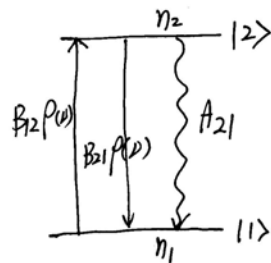
II-1. Absorption and Emission

§ Beer-Lambert law

$$I/I_0 = \exp(-\sigma n \ell) \qquad (2.1)$$

σ : absorption cross section

∴ The fraction of molecules being excited

$$= 1 - \exp(-\sigma n \ell) \qquad (2.2)$$

§ Einstein coefficients

$$\frac{dn_1}{dt} = -n_1 B_{12}\rho(\nu) + n_2\left[B_{21}\rho(\nu) + A_{21}\right] \qquad (2.3)$$

$$-\frac{dI(\nu)}{d\ell} = I(\nu)\sigma(\nu)n_1 \qquad (2.4)$$

$\rho(\nu)$: energy density per unit frequency

$(\text{erg} \cdot t^{-1}/cm^3)$

$I(\nu)$: intensity (erg/cm^2)

$$I(\nu) = \rho(\nu) \cdot c \qquad (2.5)$$

Assuming $n_2 \ll n_1$, the number density of photons being absorbed

$$-\frac{d\,I(\nu)\,d\nu}{c\,h\nu} = -dn_1 \qquad (2.6)$$

from (2.3) and (2.6)

$$\frac{I(\nu)\,d\nu\,\sigma(\nu)\,n_1\,d\ell}{c\,h\nu} = n_1\,B_{12}\,\rho(\nu)\,dt \qquad (2.7)$$

$$\rightarrow \quad B_{12} = \frac{c\,\sigma(\nu)\,d\nu}{h\nu} \qquad (2.8)$$

(where $c = d\ell/dt$ has been used)

At equilibrium $\quad dn_1/dt = 0$

$$\frac{n_2}{n_1} = \frac{B_{12}\,\rho(\nu)}{B_{21}\,\rho(\nu) + A_{21}} \qquad (2.9)$$

from (2.3), Boltzmann distribution for n_2/n_1, and the blackbody radiation distributions for $\rho(\nu)$

$$\rightarrow \quad B_{12} = B_{21}\,\frac{g_2}{g_1} \qquad \text{(microscopic reversibility)} \qquad (2.10)$$

$$A_{21} = \frac{8\pi h \nu^3}{c^3}\,B_{21} \qquad (2.11)$$

For a two level system $\quad A_{21} = \frac{1}{\tau}$

3 Franck-Condon Principle

Vibrational wavefunction overlap

$$\int \phi_{v_2}\,\phi_{v_1}\,dR$$

$$A_{21} = \frac{64\,\pi^2 \nu^3}{3\,\hbar\,c^3}\,|\mu_{21}|^2 \qquad (2.12)$$

transition dipole moment, μ_{21}

$$|\mu_{21}|^2 = \left| e \int \psi_{e_2 v_2}(r,R)\cdot\underline{r}\,\psi_{e_1 v_1}(r,R)\,dr\,d\underline{R} \right|^2 \qquad (2.13)$$

From Born-Oppenheimer approximation

$$\psi_{ev}(r,R) \cong \psi_e(r)\,\phi_v(R)$$

$$\therefore |\mu_{21}|^2 = \left| e \underbrace{\int \psi_{e_2}(r)\,\underline{r}\,\psi_{e_1}(r)\,dr}_{\text{electronic transition moment}} \cdot \underbrace{\int \phi_{v_2}(R)\,\phi_{v_1}(R)\,d\underline{R}}_{\text{F-C factor}} \right|^2 \qquad (2.14)$$
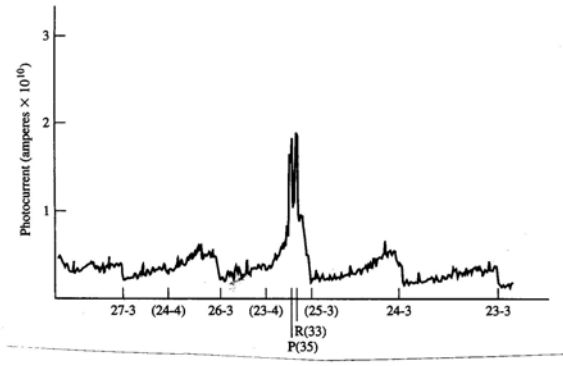
II-2 The fates of excited molecules

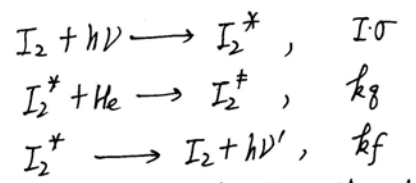Quantum yield $\equiv$ probability of events of interest per photon absorption by the system.

(A) Fluorescence / quenching
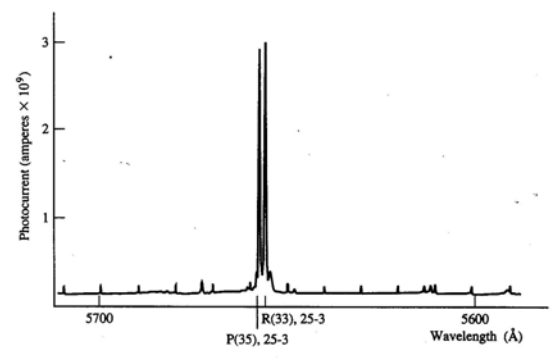
JCP 42 (1965) 3425.

$$I_2(\upsilon''=3, J''=33) + h\upsilon$$
$$\rightarrow I_2(\upsilon'=25, J'=34)$$
$$\overset{\downarrow}{\sim} h\upsilon'$$

adding He
quenching
(Stern-Volmer kinetics)

$$I_2 + h\upsilon \longrightarrow I_2^* \,, \qquad I\cdot\sigma$$
$$I_2^* + He \longrightarrow I_2^\ddagger \,, \qquad k_q$$
$$I_2^* \longrightarrow I_2 + h\upsilon' \,, \qquad k_f$$

let the fluorescence intensity with and without He be I_f and I_f°.

Homework 2

then $\dfrac{I_f^\circ}{I_f} - 1 = \dfrac{k_q[He]}{k_f}$ (prove it!)   (2.15)

(B) Internal conversion (IC) & Intersystem crossing (ISC)

$$IC \ (S_1^* \to S_0^\ddagger)$$ $$ISC \ (S_1^* \to T_1^\ddagger)$$
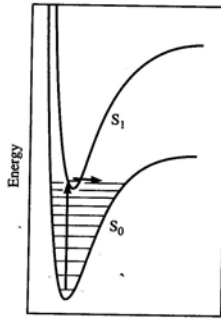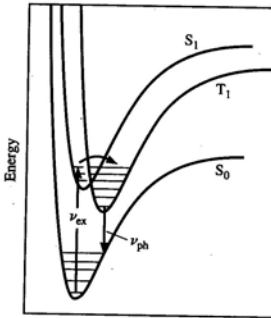
Energy redistribution can occur from one electronic state to the other electronic states (radiationless processes), often through "conical" intersections or other potential energy surface intersections.

Conserved quantities: energy, angular momentum, parity.

BUT, how do we know if IC or ISC has occurred or not?

— Compare the fluorescence lifetime with the integrated absorption cross section. This is because that if IC or ISC occurs, the measured fluorescence lifetime will be shorter than that expected from the integrated absorption cross section. (Recall (2.8), (2.11)).
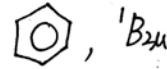
— examine the fluorescence lifetime as a function of vibrational excitation in the S_1 manifold of states

[example]   Benzene, 1st excited state $^1B_{2u}$
        fluorescence lifetime measurement under collision-free conditions.

JCP 55 (1971) 5561

⬡ , $^1B_{2u}$
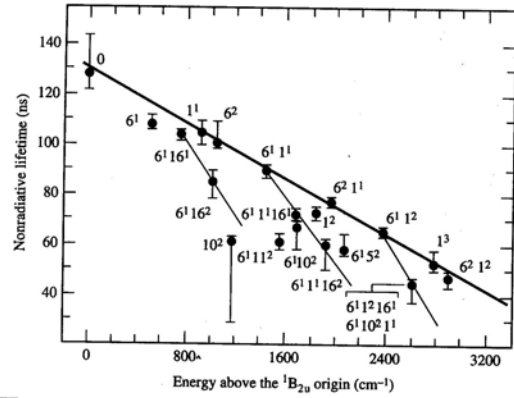
V_6 : C-C bending mode
V_1 : symmetric stretch
V_{16} : out-of-plane bend

Observation 1 : the lifetime decreases rapidly with increasing vibrational energy

Observation 2 : the lifetime decreases more dramatically with the number of quanta of V_{16}

→ the $^1B_{2u}$ state undergoes an internal conversion to the highly vibrational excited S_0 states, and V_{16} mode is a "promoting" mode.

— fluorescence quantum yield (Φ_f) measurement.

For 0^0 level of benzene, Φ_f is found to be 0.25.
From the figure, the nonradiative lifetime for the 0^0 level is 128 ns.

$$B^*(0^0) \xrightarrow{k_r} B + h\nu$$
$$ \xrightarrow{k_{nr}} B^{\ddagger}$$

k_r : radiative decay rate
k_{nr} : nonradiative decay rate
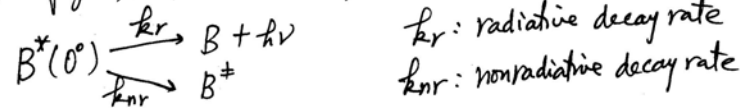
kinetically, it is a parallel process

$$k_{total} = k_r + k_{ns}$$
and $\tau_{obs.} = 1/k_{total}$

$$\therefore \; \phi_f = \frac{k_r}{k_r + k_{nr}} = 0.25$$

$$\therefore \; k_{nr} = 3\,k_r = \frac{1}{128\,ns}$$

$$k_{total} = 4\,k_r = \frac{1}{\tau_{obs.}}$$

$$\therefore \; k_r = 2.6 \times 10^6 \; sec^{-1} \qquad or \;\; \tau_r = 385\,ns$$

$$and \;\; \tau_{obs} = 96\,ns$$

(C) Intramolecular Vibrational Energy Redistribution (IVR)

In large polyatomic molecules, due to the coupling of different vibrational modes by small perturbations (anharmonicity, Fermi resonance, Coriolis couplings etc), energy can be redistributed (i.e. can flow from one mode to the other) even without collisions.

(An assumption of the RRKM theory of unimolecular dissociation)

[example] Anthracene ⬡⬡⬡

$E_v(cm^{-1})$

$\tau = 18\ ns$

766

1420

$\tau \sim 75\ ps$

1792

*

$t(ns)$ — 0 2 4 6

$\lambda(nm)$ — 340 360 380
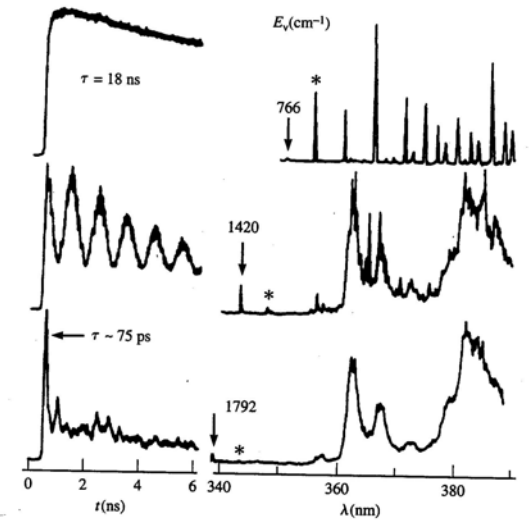
Adv. Chem. Phys.
70 (1998) 265.

low excitation :
well-resolved spectrum;
exponential decay

intermediate excitation :
complicated spectrum;
modulated decay
(quantum beat)

high excitation :
broad, lumped spectrum;
chaotic decay

(D) photodissociation

Excitation of molecules can result in dissociation into two or more fragments, i.e., a bond-breaking unimolecular reaction. It can be classified into two types: direct and indirect.

<u>Direct</u>: dissociation takes place on a single excited potential energy surface and normally it completes on the time scale of a few vibrational periods.
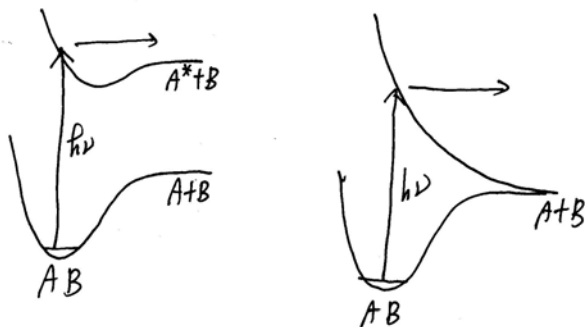
<u>Indirect</u>: dissociation involves more than one (Born-Oppenheimer approximate) potential energy surfaces. Usually it takes much longer time than the direct dissociation.
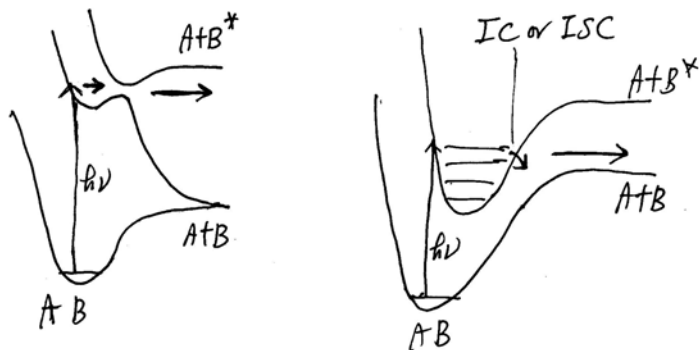
Experimental "signatures" for direct or indirect dissociation
and the underlying mechanisms

(1) fragment translational energy distribution

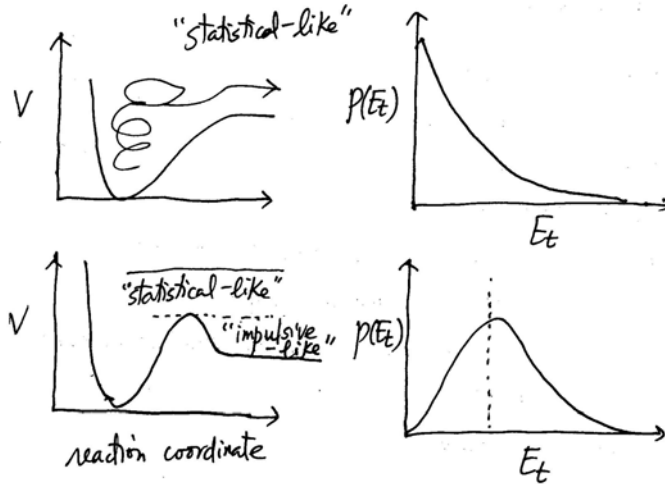direct: large kinetic energy release, normally peaks from zero

indirect: depending on the PES over which the dissociation occurs

"statistical-like"

V $P(E_t)$ E_t

"statistical-like"
"impulsive-like"

V $P(E_t)$

reaction coordinate E_t

(2) fragment angular distribution

direct: fast (compared to the rotation of the photoexcited
parent molecules, typically ~ ps)

→ anisotropic distribution

Indirect: slower or comparable to the parent rotation

→ isotropic distribution or nearly so

Let us now examine more closely the angular distribution of
a direct dissociation process.

Before the photoexcitation, the molecules are randomly distributed in all directions. A linearly polarized light is used to photodissociate the molecule. Upon the absorption of the photon, the excited molecules have a preferred direction according to the excitation probability of $|\mu \cdot E|^2$, where μ is the transition dipole moment and E is the electric field of the light. Thus, the photoexcited molecules will have a distribution of alignments proportional to $\cos^2\theta$, θ is the angle between μ and E. If the excited molecule will dissociate very rapidly compared to its rotational time scale, then the recoil velocity v of the fragment, which has a fixed relationship to the transition dipole μ, will also be aligned. For example, $AB \xrightarrow{h\nu} A+B$, if μ is along the A-B bond axis, a fast direct dissociation will lead to a recoil angular distribution of $\cos^2\theta$

In general, $I(\theta) = \frac{1}{4\pi}[1 + \beta P_2(\cos\theta)]$

where $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ is the second Legendre polynomial and $\beta = 2 P_2(\cos\chi)$ with χ as the angle between μ and the recoil direction v. The value of β, the anisotropy parameter, lies between -1 and 2. Considering the limiting cases:

$\beta = 2 \quad \therefore \cos\chi = 1 \quad$ i.e. $\mu \parallel v, \quad I(\theta) = 3\cos^2\theta$

$\beta = -1 \quad \therefore \cos\chi = 0 \quad$ i.e. $\mu \perp v, \quad I(\theta) = \frac{3}{2}\sin^2\theta$

So, the angular distribution, or the β-value, can provide information about the direction of the transition dipole μ which in turn can tell us about the symmetry of the electronic excited state.

BUT, if the parent molecule rotates before dissociation, the alignment of the recoil velocity with respect to the polarization direction of the dissociating light, i.e., the β-value, will be reduced substantially. $\longrightarrow$ lifetime of dissociation process.

Summary of a few key concepts

(1) A complex reaction, such as a chain reaction, and a homogeneous catalysis etc, always consists of many elementary chemical reactions. To interpret the empirical rate law and other experimental observation, a reaction mechanism is proposed with a set of coupled rate equations. To validate the proposed reaction mechanism, one can apply steady state approximations to the reaction intermediates (or using the computer to solve the coupled differential equations numerically) for a consistent rate law. However, even if the proposed reaction mechanism agrees with experiments, it will not be unique; as more data become available, additional reactions may need to be added to the reaction mechanism to account for the new observations.

(2) Photoexcitation of a molecule can induce many competing processes

Typical time scales

  fluorescence : $10^{-9} - 10^{-6}$ s
  phosphorescence : $10^{-4} - 100$ s
  IC / ISC : $10^{-12} - 10^{-4}$ s
  direct dissociation : $10^{-14} - 10^{-13}$ s
  indirect dissociation : $10^{-12} - > 10^{-6}$ s
      (depending on the size of the parent)

Modern-day's experimental techniques enable the real-time measurement even for a direct photodissociation process
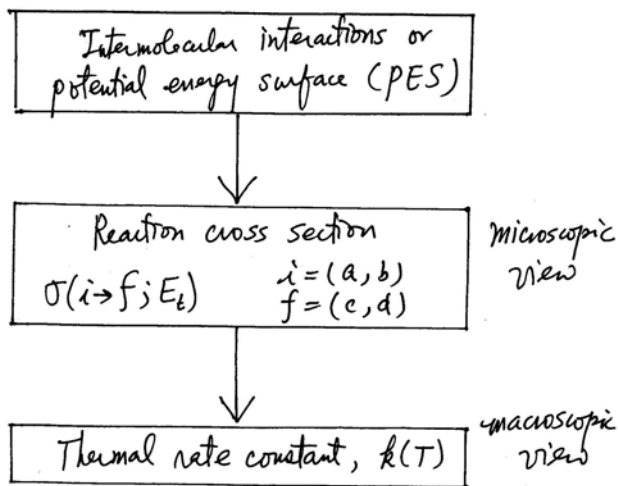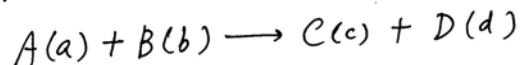 $\rightarrow$ femtochemistry

BUT, recalling the uncertainty principle, $\Delta E \cdot \Delta t \leq \hbar$!
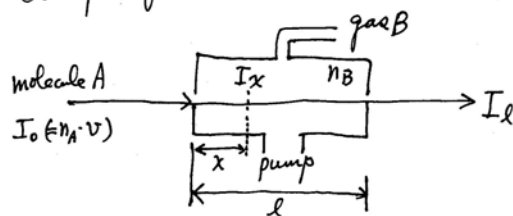
III. Molecular Reaction Dynamics

Overview : What is reaction "dynamics"?

— A microscopic (or molecular) view of a chemical transformation (i.e. how the bond-breaking and bond-forming processes take place).

$$A(a) + B(b) \longrightarrow C(c) + D(d)$$

```
┌─────────────────────────────────┐
│  Intermolecular interactions or │
│  potential energy surface (PES) │
└─────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────┐
│   Reaction cross section        │     microscopic
│                                 │       view
│   $\sigma(i \to f; E_t)$    $i = (a,b)$ │
│                     $f = (c,d)$ │
└─────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────┐
│  Thermal rate constant, $k(T)$  │     macroscopic
└─────────────────────────────────┘           view
```

III−1. Concept of σ

molecule A

$I_0 (= n_A \cdot v)$

I_x n_B gas B $\longrightarrow I_\ell$

x pump

ℓ

In analogy to a beam of light attenuated by absorption (Beer-Lambert law), the initial beam flux (I_0, in molecule/cm²s) is attenuated by collisions with the target molecule B.

$$I_x = I_0 \exp(-x/\lambda) \tag{3.1}$$

where λ = mean free path (the average distance a molecule travels between collisions).

Since the probability of a beam of molecule A undergoing a collision in the interval x to $x+\Delta x$ is given by $\Delta x/\lambda$ and it should also be proportional to the number density n_B of the target molecule B, we have $\Delta x/\lambda \propto n_B \Delta x$. The collisional cross section σ is taken to be the proportional constant such that

$$1/\lambda \equiv \sigma n_B \tag{3.2}$$

Equation (3.1) becomes $I_x = I_0 \exp(-\sigma n_B x)$

the dimension of σ is area/molecule, e.g. cm^2/molecule

A typical gas kinetic cross section $\sim 30 \overset{\circ}{A}{}^2$ or 2×10^{-10} cm^3/molecule$\cdot$s

or $\sim 6\times10^6$ torr^{-1}s^{-1}

III-2. Relationship between σ and k

$I(x) - I(x+\Delta x)$ corresponds to the decrease of the beam intensity in a volume enclosed by two unit areas separated by a distance Δx, so the number of A–B collisions per unit volume per unit time is

$$[I(x) - I(x+\Delta x)]/\Delta x = -\frac{dI}{dx}$$

This is also a rate and can be expressed as

$$-dI/dx = -dn/dt = k\, n_A n_B \tag{3.3}$$

$$\text{where} \quad n_A(x) = I(x)/v \tag{3.4}$$

From (3.1) and (3.2) one obtains

$$-dI/I\,dx = -d\ln I/dx = \frac{1}{\lambda} = \sigma n_B$$

From (3.4) $\quad -dI/dx = I\cdot\sigma n_B = \sigma v\, n_A n_B \tag{3.5}$

Compared (3.3) and (3.5), $\longrightarrow \quad k = \sigma v \tag{3.6}$

Equation (3.6) refers to collisions for which the relative velocity is well-defined both in magnitude and direction.

BUT, the thermal rate constant $k(T)$ refers to the rate
coefficient at the temperature T; thus, need to perform Boltzmann
averaging of equation (3.6). If the velocities of A and B are
described by Maxwell-Boltzmann distributions

$$f(v;T) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-mv^2/2kT\right)$$

then

$$k(T) = \left(\frac{\mu}{2\pi kT}\right)^{3/2} \int_0^\infty v\,\sigma(v)\exp\left(-\mu v^2/2kT\right) 4\pi v^2\, dv \qquad (3.7)$$

or

$$= \frac{1}{kT}\left(\frac{8}{\pi\mu kT}\right)^{1/2} \int_0^\infty E_t\,\sigma(E_t)\exp\left(-E_t/kT\right) dE_t \qquad (3.8)$$

where $E_t = \frac{1}{2}\mu v^2$ and $\mu = m_A m_B/(m_A+m_B)$ is the reduced mass
of A+B.

Quantum mechanically, an atom or a molecule has
quantized internal energy level structures. The most fundamental
quantity at the integral cross section level of detail is the
state-to-state one, $\sigma(i \to f; E_t)$. The total collisional cross
section can be expressed as

$$\sigma(E_t) = \sum_i F_i \sum_f \sigma(i \to f; E_t) \qquad (3.9)$$

where E_t: the relative translational energy of two reactants.
$\qquad$ F_i: normalized population factor of reactants in the
$\qquad\qquad$ state of $i = (a, b)$.

III-3. Reaction probability and the impact parameter

Equation (3.9) gives the collisional cross section. The reaction
cross section refers to the rate of those collisions which lead to
a chemical reaction. It is a measure of the effective size of the
molecules as determined by their propensity to react. Thus, it is
necessarily smaller than the collisional cross section which governs
the rate of all collisions, irrespective of their outcomes. The ratio
of $\sigma_{rx}/\sigma_{Total}$ is then a rough measure of the reaction probability.

To gain further insights into reaction probability, we will introduce the concept of impact parameter, b, which is the distance of closest approach of the two molecules, in the absence of interactions.
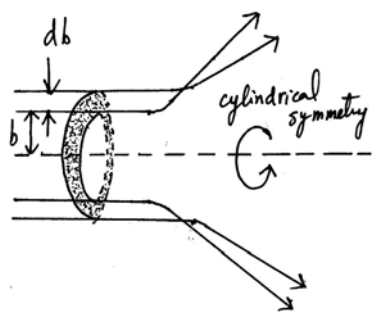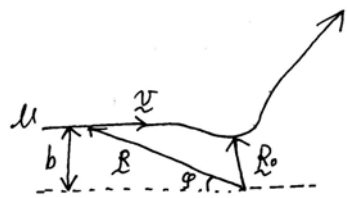
For a given initial energy and impact parameter, the collisional trajectory is uniquely specified — at least classically. If the molecules are randomly oriented in space, then the collisions with impact parameters in the range of b to $b+db$ are equally probable. The corresponding cross section, i.e., the effective area, is

$$d\sigma = 2\pi\, b\, db \qquad (3.10)$$
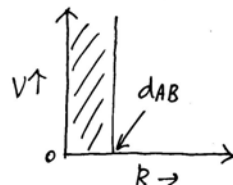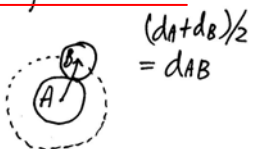
$$\sigma = 2\pi \int b\, db$$

(3.10) assumes the collision has unit probability to reaction, which is not necessarily be the case. In general, we define the reaction probability $P(b)$, or the opacity function, as the fraction of collisions with impact 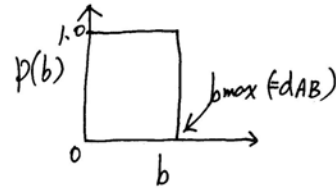parameter b that leads to reaction. Two features regarding $P(b)$: (i) $0 \le P(b) \le 1$ and (ii) $P(b) \to 0$ as b becomes large ($\to \infty$), thus $\sigma_R = 2\pi \int_0^\infty P(b) \cdot b\, db$. (3.11)

III-4. A few simple collision models

(A). Hard-sphere model

$(d_A + d_B)/2 = d_{AB}$

In terms of opacity function

$$p(b) = 1 \quad b \leq b_{max}$$
$$= 0 \quad b > b_{max} \qquad (3.12)$$

(3.11) & (3.12) lead to $\qquad \sigma_R = \pi b_{max}^2 \qquad (3.13)$

So, σ_R is a constant, independent of collision energy and the internal states. From equation (3.7) or (3.8), one has

$$k(T) = [8/\pi\mu(kT)^3]^{1/2} \int_0^\infty E \cdot (\pi b_{max}^2) \exp(-E/kT) dE$$
$$= b_{max}^2 (8\pi kT/\mu)^{1/2} \qquad (3.14)$$

i.e., a $\sqrt{T}$-dependence. Clearly, this is a too simple model to account for the usual Arrhenius behavior, $k(T) = A \exp(-Ea/kT)$.

(B) Modified hard-sphere model

The simplest modification to the above model is to add another constraint for reaction, i.e.,

$$\sigma_R(E) = 0 \qquad E < E_0 \qquad (3.15)$$
$$= \pi b_{max}^2 \qquad E \geq E_0$$

Then, $k(T) = [8/\pi\mu(kT)^3]^{1/2} \int_{E_0}^\infty E \cdot (\pi b_{max}^2) \exp(-E/kT) dE$

$$= (8\pi kT/\mu)^{1/2} b_{max}^2 (1 + E_0/kT) \exp(-E_0/kT) \qquad (3.16)$$

BINGO! (3.16) is very much like an Arrhenius form. BUT, it does not appear to be reasonable in that E_0 is the same for all values of b. Intuitively, a "head-on" collision (smaller b) may have a greater chance to react than a "grazing" one (larger b).
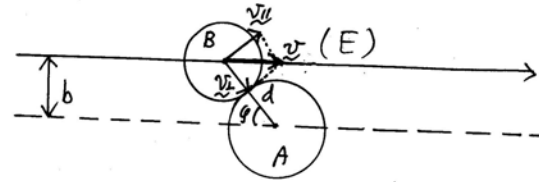
$$E = \tfrac{1}{2}\mu v^2 = \tfrac{1}{2}\mu(v_\perp^2 + v_{//}^2) \qquad (3.17)$$

The first term is the collision energy along the line of centers, which is assumed in the model to be effective in bring about reaction, and the second term is the centrifugal energy.

Since $\quad v_\perp = v \cos\varphi \qquad\qquad (3.18)$

and $\quad \cos\varphi = \sqrt{d^2 - b^2}/d \,. \qquad (3.19)$
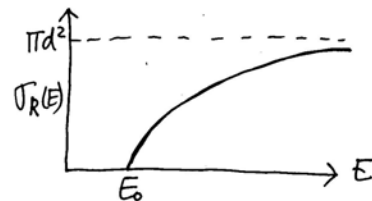
then $\quad E_\perp = E(1 - b^2/d^2) \qquad (3.20)$

The model now requires $E_\perp \geq E_0$ for reaction to occur,

i.e., $\quad (E - E_0 - E b^2/d^2) \geq 0 \qquad (3.21)$

We take b_{max} as the largest value of b that satisfies (3.21),

so $\quad b_{max} = d(1 - E_0/E)^{1/2} \qquad (3.22)$

or $\quad \sigma_R = \pi b_{max}^2 = \begin{cases} 0 & , E \leq E_0 \\ \pi d^2(1 - E_0/E), & E > E_0 \end{cases} \qquad (3.23)$

Physically, a more reasonable energy dependence — no longer the step-function dependence.

$$\therefore k(T) = (8/\pi\mu(kT)^3)^{1/2} \int_{E_0}^{\infty} \pi d^2 (E - E_0) \exp(-E/kT)\, dE$$

$$= (\pi d^2)(8kT/\pi\mu)^{1/2} \exp(-E_0/kT) \qquad (3.24)$$

(3.24) can be viewed as the product of three terms,

(hard sphere σ)(mean $\bar{v}(T)$)·(Arrhenius factor).

The activation energy, E_a, is

$$E_a \equiv -K \frac{d \ln k}{d(1/T)} = \frac{1}{2} KT + E_0 \qquad (3.25)$$

The major problem with this model is that the observed pre-exponential factor is often much smaller than the hard-sphere collision rate. At least two reasons for that: (i) It is still a hard sphere model by nature; the intermolecular interaction is ignored. (ii) Intuitively, one may expect that the activation barrier height will depend on the orientation of the reagents due to the anisotropic interaction potential.
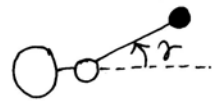
i.e., $E_0(\gamma)$

the steric effects !

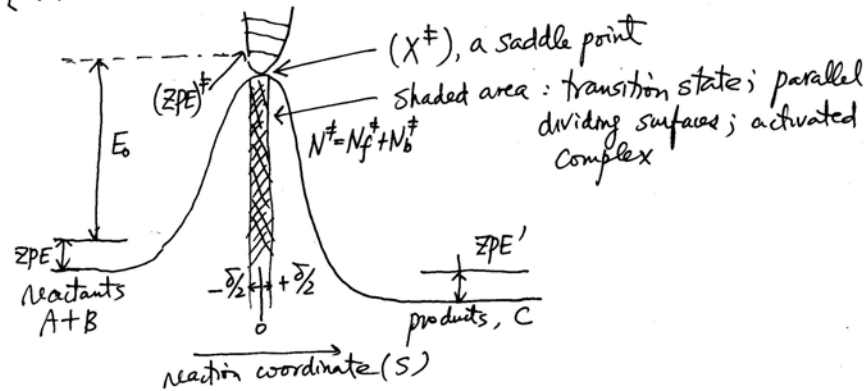## III-5. Transition State Theory (TST or ACT)

The first theoretical attempt to determine the absolute reaction rates, introduced by Eyring, Evans and Polanyi in 1935, and discussed more deeply by Wigner in 1938. There are many ways to derive the expression of TST. All of them are based on (i) Born-Oppenheimer approximation which separates the electronic and nuclear motions; and (ii) canonical ensemble, i.e., the reactant molecules are distributed among their states in accordance with Maxwell-Boltzmann distribution. In addition, there are few assumptions in most of textbooks. We will introduce the assumptions and then use the simplest approach (i.e., the least rigorous way) to derive the TST.

(A) Assumptions in canonical TST.

(i) Molecular systems that have crossed the transition state in the direction of products can not turn around and reform reactants (i.e., no re-crossing; a "point of no return").

(ii) At transition state, motion along the reaction coordinate may be separated from the other motions and treated classically as a translation.

(iii) Even in the absence of an equilibrium between reactant and product 23 molecules, the transition states that are becoming products are distributed among their states according to the Maxwell–Boltzmann laws (i.e., a "quasi-equilibrium hypothesis"),

[It can be shown that (iii) is not necessary since it follows from (ii)]

$(X^{\ddagger})$, a saddle point

Shaded area : transition state; parallel dividing surfaces; activated complex

$N^{\ddagger} = N_f^{\ddagger} + N_b^{\ddagger}$

$(ZPE)^{\ddagger}$

E_0

ZPE

reactants
A+B

$-\delta/2 \leftrightarrow +\delta/2$

0

ZPE'

products, C

reaction coordinate (S)

(B) Derivation of TST

The simplest approach is based on a kinetic model

$$A+B \xrightleftharpoons[k_{-1}]{k_1} X^{\ddagger} \xrightarrow{k_2} C \qquad (3.26)$$
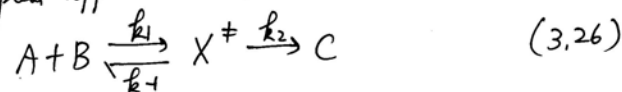
$$\frac{d[C]}{dt} = k_2 [X^{\ddagger}] \qquad (3.27)$$

$$= [k_2 k_1/(k_{-1}+k_2)] [A][B] \quad \text{Why?} \quad (3.28)$$

$$\simeq (k_2 k_1/k_{-1}) [A][B] \quad \text{Why?} \quad (3.29)$$

Recalling k_1/k_{-1} is the equilibrium constant for $A+B \rightleftharpoons X^{\ddagger}$

Using statistical thermodynamics,

$$d[C]/dt = k_2 \frac{Q_{Tot}^{\ddagger}}{Q_A Q_B} \exp(-E_0/kT) [A][B] \qquad (3.30)$$

where $Q_{Tot}^{\ddagger}$ is the total partition function per unit volume of the transition state $X^{\ddagger}$, Q_A & Q_B are those for the reactants, and E_0 is the lowest energy level of the transition state relative to that of the reactants. [The partition function is the number of states that are available to the system at a given temperature, $q \equiv \sum_n \exp(-E_n/kT)$.]

<u>What is k_2?</u>

From (3.27) $d[C]/dt = k_2[X^\ddagger] = k_2 N_f^\ddagger = (k_2/2)N^\ddagger$ (3.31)

where $N_f^\ddagger = N_b^\ddagger = N^\ddagger/2$ (from assumption (i), why?) has been used.

From assumption (ii'), $k_2 = \bar{v}_s / 2\delta$ (3.32)

$\bar{v}_s$ is the average velocity (1-dim) along the reaction coordinate (s)

$$\bar{v}_s = (2KT/\pi \mu_s)^{1/2} \qquad (3.33)$$

and $\mu_s \equiv$ reduced mass for motion through the dividing surface with width δ. Inserting (3.32) into (3.30), then

$$\frac{d[C]}{dt} = \left(\frac{2KT}{\pi \mu_s}\right)^{1/2} \frac{1}{2\delta} \frac{Q_{Tot}^\ddagger}{Q_A Q_B} \exp(-E_0/KT) [A][B] \qquad (3.34)$$

<u>What are μ_s and δ?</u>

From assumption (ii) $Q_{Tot}^\ddagger = Q_s \cdot Q^{\ddagger\prime}$ (3.35)

Where Q_s is the partition function for motion along reaction coordinate, and $Q^{\ddagger\prime}$ is that for all other $3N-7$ degrees of freedom of the transition state. On "particle-in-box" model, it can be shown that

$$Q_s = (2\pi \mu_s KT)^{1/2} \delta/h \qquad (3.36)$$

Inserting (3.35) and (3.36) into (3.34)

$$\frac{d[C]}{dt} = \frac{KT}{h} \frac{Q^{\ddagger\prime}}{Q_A Q_B} \exp[-E_0/KT][A][B] \qquad (3.37)$$

but kinetically, $\frac{d[C]}{dt} = k[A][B]$

Thus, $\boxed{k_{TST} = k_{abs.} = \frac{KT}{h} \frac{Q^{\ddagger\prime}}{Q_A Q_B} \exp(-E_0/KT)}$ (3.38)

Note that δ, μ_s etc are cancelled out in (3.38), what a miracle!

(C) A few comments on TST.

(i) TST is not just for bimolecular reaction, it is also applicable to unimolecular reaction, except (3.38) becomes

$$k_{uni} = \frac{KT}{h} \frac{Q^{\ddagger\prime}}{Q_A} \exp(-E_0/KT) \qquad (3.39)$$

(ii) the physical meaning of (3.38)

$$k_{TST}(T) = \frac{kT}{h} \frac{Q^{\ddagger\prime}}{Q_A Q_B} \exp(-E_0/kT) \qquad (3.38)$$

The factor $\frac{kT}{h}$ is typically $\sim 6 \times 10^{12} s^{-1}$ at room temperature. Recalling the partition function for a harmonic oscillator, $Q_v \cong \frac{kT}{h\nu}$, thus, $\frac{kT}{h}$ can be viewed as the frequency at which the reactants attempt to get to the transition state.

The factors $\frac{Q^{\ddagger\prime}}{Q_A Q_B} \exp(-E_0/kT)$ determine the ratio of the number of states available to the activated complex (less one degree of freedom) divided by the number of states available to the reactants. The reaction rate, k_{TST}, is just the frequency-of-attempt times this ratio. BUT, k_{TST} is the upper bound to the true k. (why?)

(iii) A thermodynamic view of the TST rate constant (more widely used in solution phase kinetics)

Re-expressing (3.38) as $\quad k_{TST} = \frac{kT}{h} K^{\ddagger\prime} \qquad (3.40)$

where $\quad K^{\ddagger\prime} = \frac{Q^{\ddagger\prime}}{Q_A Q_B} \exp(-E_0/kT) \qquad (3.41)$

$K^{\ddagger\prime}$ can be thought as a sort of equilibrium constant describing the ratio of the activated complexes (less one degree of freedom) to reactants. Recalling Gibbs free energy

$$-RT \ln K^{\ddagger\prime} = \Delta G^{\ddagger} \qquad (3.42)$$

$$\therefore \quad k_{TST}(T) = \frac{kT}{h} \exp(-\Delta G^{\ddagger}/RT) \qquad (3.43)$$

$$= \frac{kT}{h} \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT) \qquad (3.44)$$

where $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ = the change in Gibbs free energy in going from the reactants to the activated complexes.

In the case of an ideal gas, as an example,

$$\Delta H = \Delta(E + pV) = \Delta E + \Delta nRT \qquad (3.45)$$

for $A + B \rightleftharpoons X^{\ddagger} \qquad \Delta n = -1$

$$\therefore \quad \Delta H^{\ddagger} = \Delta E^{\ddagger} - RT \qquad (3.46)$$

and $\Delta E^{\ddagger}$ is the activation energy in going from reactants to activated complexes

i.e. $\Delta E^{\ddagger} = Ea$

$\therefore k_{TST}(T) = \dfrac{KT}{h} \exp\left(\dfrac{\Delta S^{\ddagger}}{R}\right) \cdot e^{1} \cdot \exp(-Ea/RT)$ (3.47)

Compared to the Arrhenius form $k = A \exp(-Ea/RT)$,

one has $A = \dfrac{KT}{h} e^{1} \exp(\Delta S^{\ddagger}/R)$ (3.48)

So, the pre-exponential factor A corresponds to an entropy of activation. For a bimolecular reaction, $\Delta S^{\ddagger}$ is always a negative quantity (why?). Smaller A means $\Delta S^{\ddagger}$ more negative, or the activated complex is more "ordered". In collision models, the steric factor is much smaller than unity. In TST, there are few accessible states of the complexes.

III-6. Statistical (or Tolman) interpretation of Ea

In general, the thermal rate constant can be expressed as

$$k(T) = \int_0^{\infty} k(E) \exp(-E/kT)/Q \; dE \qquad (3.49)$$

where $Q = Q_t Q_I$ is the canonical partition function of the reactants.

The experimental (Arrhenius) Ea is defined as

$$Ea \equiv -K \frac{d \ln k(T)}{d(1/T)}$$

$$= \frac{\int_0^{\infty} E \, k(E) \exp(-E/kT) dE}{\int_0^{\infty} k(E) \exp(-E/kT) dE} + K \frac{d \ln Q}{d(1/T)}, \quad \text{(prove it)} \quad (3.50)$$

The second term is the average energy of the reactants (why?),

$$\text{ie } \langle E \rangle = -K \frac{\ln Q}{d(1/T)} = \langle E_t \rangle + \langle E_I \rangle = \tfrac{3}{2} KT + \langle E_I \rangle \qquad (3.51)$$

The first term is the average energy of the distribution $k(E)\exp(-E/kT)$. Thus, it is the average energy of "the group of reactants which undergo reaction", denoted as $\langle E^* \rangle$

$$\therefore \quad Ea = \langle E^* \rangle - \langle E \rangle \qquad (3.52)$$

         ↑   ↖

  average energy   average energy

of "reacting" reactants   of all reactants.
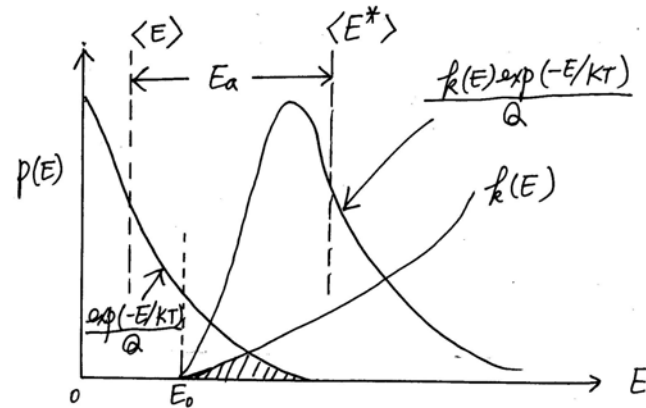
Note (i) It is often the case that $E_0 > \langle E \rangle$, so that only the Boltzmann tail in the post threshold energy region contributes to the magnitude of $k(T)$.

(ii) There is a rough correspondence (but not identical) of the activation energy (E_a) with the threshold energy (E_0). The latter, E_0, is not necessarily the same as the height of the potential energy barrier, E_b.
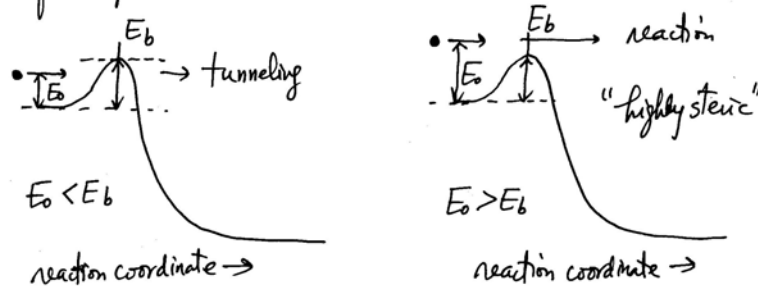
III-7.   Potential energy surface (PES)

Born-Oppenheimer approximation :   separation of electronic and nuclear motions due to the large disparity in time scales.

→ The chemical reaction is envisioned as the nuclear motions over the electronic (potential) energy surface.

simple collision model : <u>height</u> of the barrier to reaction.

Transition state theory : the <u>shape</u> of PES in the vicinity of the saddle point (the transition state) in order to calculate the partition function for $X^{\ddagger}$.

Reaction dynamists try to understand chemical reactivity at the molecular level (i.e., beyond just the thermal rate constant $k(T)$).

— What is the energy distribution of reaction products?

— Is translational energy more effective in promoting a reaction than the vibrational energy of reactants?

- - - - - - - - - - - - - - - - -

So, need to know more about PES — not just near the transition state region, and about the relationship between the features of PES and the dynamics consequence.

e.g. barrier location? potential well? mass effects? - - - -

(A) Some microscopic mechanisms and typical profiles of the reaction path

<u>Microscopic mechanisms</u>

(i) direct reaction (abstraction reaction)
   — "simultaneous" (old) bond-breaking and (new) bond forming
   e.g. $F + H_2 \rightarrow HF + H$
   $K + CH_3I \rightarrow KI + CH_3$
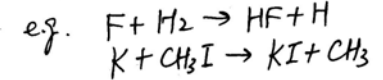
(ii) indirect reaction (complex-forming reaction)
   — sequential steps in bond formation and bond rupture

(the distinction between (i) and (ii) is the time scales; the internal motion is used as the time clock.)

(a) Insertion reaction — upon complex formation, two new bonds and one old bond are simultaneously formed and broken, respectively.
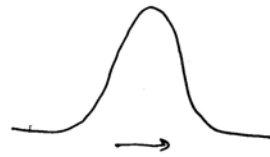   e.g. $O(^1D) + CH_4 \rightarrow (CH_3OH)^{\ddagger} \rightarrow CH_3 + OH$
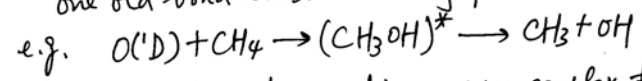
(b) addition-elimination reaction — upon complex formation, only one new bond is formed.
   e.g. $O(^3P) + C_2H_4 \rightarrow (OC_2H_4)^{*} \rightarrow OC_2H_3 + H$
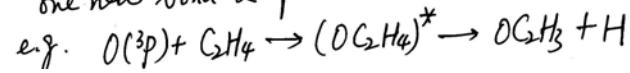
Typical profiles of reaction path.

(i) molecule + molecule

direct reaction

e.g. $H_2 + D_2 \rightarrow 2HD$
$E_a \gtrsim 70$ kcal/mol

(ii) radical + saturated molecule

e.g. $OH + H_2 \rightarrow H_2O + H$
$E_a \simeq 4$ kcal/mol
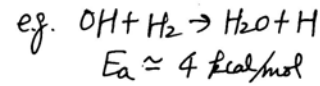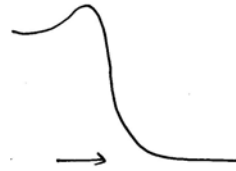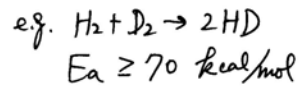
(iii) radical + unsaturated molecule

indirect reaction

e.g. $OH + CO \rightarrow (HOCO)^{\ddagger} \rightarrow CO_2 + H$
$E_a \gtrsim 0$ kcal/mol

(iv) radical + radical

"capture reaction"

$O + OH \rightarrow (HO_2)^{\ddagger} \rightarrow H + O_2$
$E_a \simeq -0.2$ kcal/mol
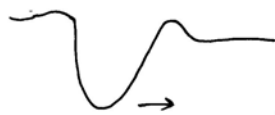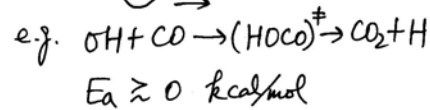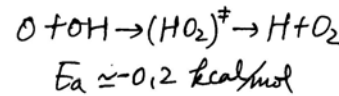
Two-dim. contour plot of PES.

(a)

Reactants
Transition State
Intermediate
Transition State
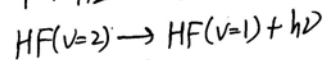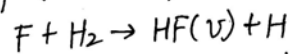Products
$V(q_1, q_2)$

(b)

R
TS
S
P
q_1
q_2
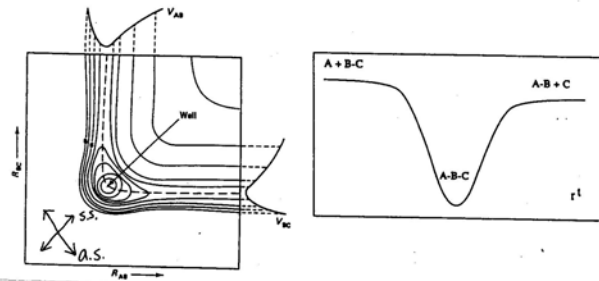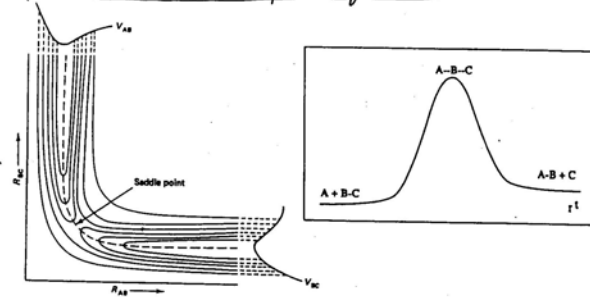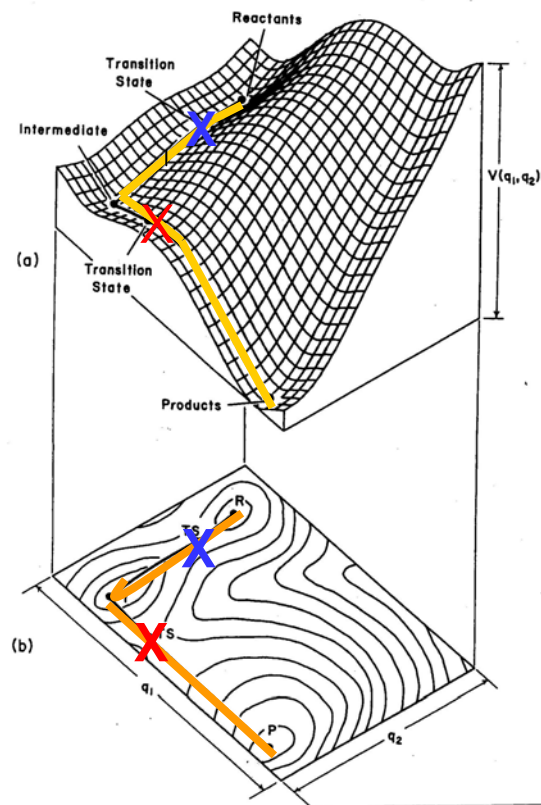
@ 3-D representation of PES.
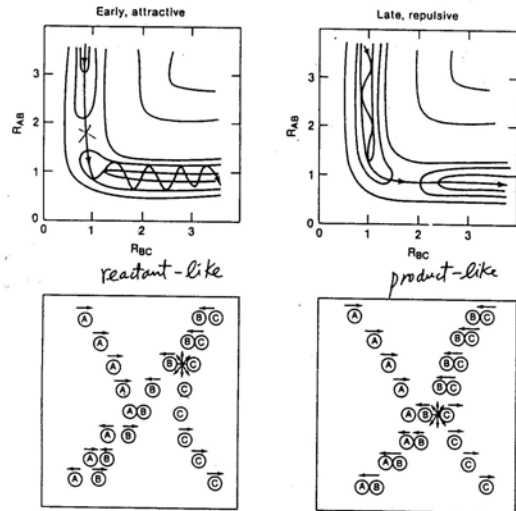
(B) Activated reaction — a reaction with barrier

[example] The key reaction for the chemical laser

$$F + H_2 \rightarrow HF(v) + H$$
$$HF(v=2) \rightarrow HF(v=1) + h\nu$$

the HF product is highly vibrationally excited, peaking in $v=2$ (a population inversion)

why ?

F+H₂

———— $v=3$

———— $v=2$

———— $v=1$

———— $v=0$

HF(v)+H

$$A + BC \rightarrow AB + C$$

Early, attractive | **Late, repulsive**

(figures: contour plots with R_{AB} vs R_{BC})

reactant-like | product-like

(figures: X-shaped diagrams)
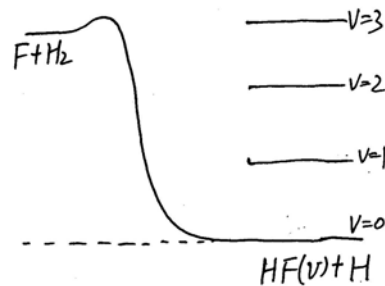
Polanyi's rule
(Effects of barrier location)

Early barrier:
The reaction exoergicity is released while A and BC are approaching each other (attractive energy release)
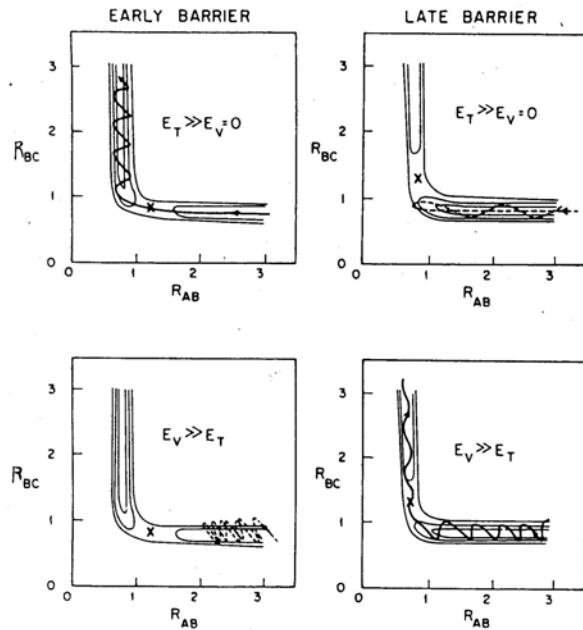→ vibrational excitation of the AB product.

Late barrier:
The energy is released as AB rebound from C (repulsive energy release)
→ translationally hot products.

One step further: energy disposal $\overset{?}{\longleftrightarrow}$ energy requirement
(microscopic reversibility)

Not all forms of energy are equally effective in driving chemical reactions!

EARLY BARRIER | **LATE BARRIER**

$E_T \gg E_V = 0$ | $E_T \gg E_V = 0$

$E_V \gg E_T$ | $E_V \gg E_T$

(figures: contour plots with R_{AB} vs R_{BC})

Can one extend the use of Polanyi's rule to other analogous reactions? Yes!

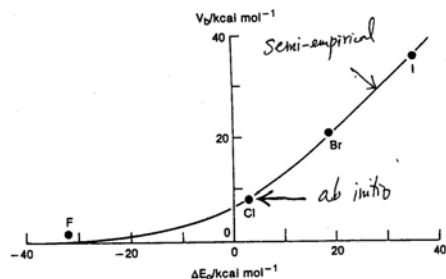Hammond's postulate (1955) or Evans-Polanyi relationship (1938):

In a series of analogous reactions, the more exoergic the reaction, the more the transition state will resemble the reactants in structure and the lower the barrier will be.
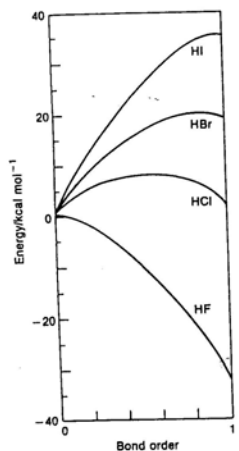
Isr. J. Chem. 19 (1980) 330.

$$X + H_2 \rightarrow HX + H$$
$$(X = F, Cl, Br, I)$$
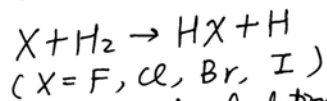
semi-empirical calculation of bond order and the barrier height.

(C) Capture reactions
 — applicable to many ion+molecule and radical+radical reactions
 — no barrier; the reaction is governed by long-range attraction and often forms an intermediate complex.

(i) Concept of centrifugal energy

Consider a two-particle collision, Newton pointed out that it (a central force system) requires the angular momentum ($\ell \equiv \mu \underline{R} \times \dot{\underline{R}}$) being conserved. There are correspondingly two terms in the kinetic energy of the relative motion,

$$T = \tfrac{1}{2}\mu \dot{\underline{R}}^2 = \tfrac{1}{2}\mu \dot{R}^2 + \ell^2/2\mu R^2 \qquad (3.53)$$

Recalling the impact parameter b, $\quad \ell = \mu v b \qquad (3.54)$

$$\text{and}\quad T = \tfrac{1}{2}\mu \dot{R}^2 + E_T b^2/R^2 \qquad (3.55)$$

where $E_T = \frac{1}{2}\mu v^2$ (v = initial relative velocity of the colliding reactants).[33]

During the collision, as R decreases, the kinetic energy that is wholly translational, is being converted into centrifugal energy, $E_T b^2/R^2$, at the expense of the first term (the radial kinetic energy). The total energy of the system is

$$E_T = T + V(R) = \frac{1}{2}\mu\dot{R}^2 + E_T b^2/R^2 + V(R) \qquad (3.56)$$

Two ways to view the centrifugal energy:

(a) grouping it into kinetic energy

$$E_T(1 - b^2/R^2) = \frac{1}{2}\mu\dot{R}^2 + V(R) = E_\perp \qquad (3.57)$$

The approach motion of the two molecules is thus equivalent to that of a particle of mass μ moving in a potential $V(R)$ with an effective kinetic energy (i.e. the energy along the line of centers) equal to $E_T(1 - b^2/R^2)$. The larger b is, the smaller is this "effective" kinetic energy. This is the view we used in III-4.(c) for the line-of-centers model.

(b) grouping it into potential energy, as an effective potential

$$V_{eff}(R) = V(R) + E_T b^2/R^2 \qquad (3.58)$$

The centrifugal energy now acts as a repulsive contribution to V_{eff} (i.e. a centrifugal barrier) in that it prevents the too-close approach of the colliding molecules. As the two molecules approach each other, their centrifugal energy (due to the relative rotation of the two molecules) $E_T b^2/R^2$ increases at the expense of the potential and the radial kinetic energy ($\because$ total energy is conserved). Eventually, they reach the smallest separation R_0, the turning point or the distance of closest approach, which is the point where $\dot{R} = 0$. Thus,
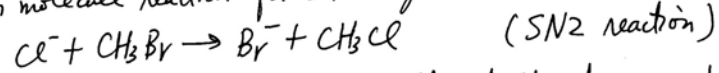
$$E_T = V(R_0) + E_T b^2/R_0^2 \qquad (3.59)$$
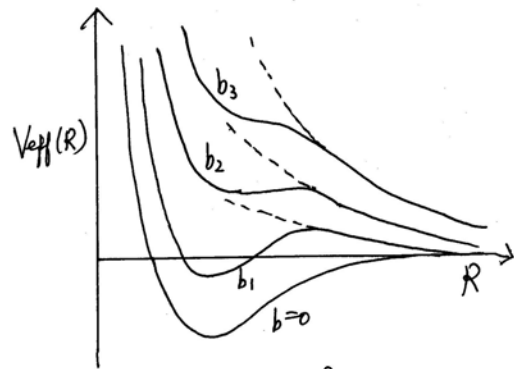
Here, $b_3 > b_2 > b_1 > 0$

Note the bumps in $V_{eff}(R)$ for $0 \leq b \leq b_2$. The dashed lines are for $V=0$

(ii) Langevin (1905) model

With the concept of centrifugal energy (barrier), let us consider an ion molecule reaction for estimating its reaction rate.
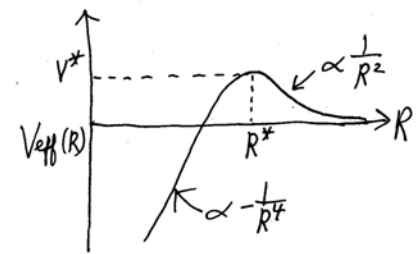
$$Cl^- + CH_3Br \longrightarrow Br^- + CH_3Cl \qquad (SN2 \text{ reaction})$$

Cl^- and CH_3Br interact at long range through the charge and induced dipole interaction (a reaction without threshold)

$$V(R) = -\frac{1}{2} \frac{\alpha e^2}{R^4} \qquad (3.60)$$

α: polarizability of the neutral molecule CH_3Br, and $\bar{e} = 4.8 \times 10^{-10} esu$

$$V_{eff}(R) = V(R) + l^2/2\mu R^2 = -\frac{1}{2} \frac{\alpha e^2}{R^4} + \frac{Eb^2}{R^2} \qquad (3.61)$$

To find the maximum of V_{eff}, i.e. the location of the centrifugal barrier, R^+, $dV_{eff}/dR = 0$ at R^* (3.62)

The criterion for reaction is that the molecules must reach R^* with at least some kinetic energy left for reaction to occur,

$$E - V_{eff}(R^*) = 0 \qquad (3.63)$$

From (3.62)
$$R^{*} = (\alpha e^2/E)^{1/2}/b \qquad (3.64)$$
$$V_{eff}(R^*) = E^2 b^4/2\alpha e^2 \simeq E \qquad (3.65)$$

So the critical impact parameter bmax is
$$b_{max} = (2\alpha e^2/E)^{1/4} \qquad\qquad (3.66)$$

$$\sigma_L = \pi b_{max}^2 = \pi(2\alpha e^2/E)^{1/2} \qquad\qquad (3.67)$$

For a typical small polyatomic molecule
$$\alpha \cong 3\times10^{-24} \; cm^3$$
at room temperature $\quad E = KT \cong 4\times10^{-14} \; erg/molecule$

Langevin model leads to
$$\sigma_L \cong 2\times10^{-14} \; cm^2 \simeq 200 \, \mathring{A}^2 \quad (larger \; than \; hard\text{-}sphere \; \sigma \,!)$$

, which is very close to experimental values.

The model also predicts that the reaction cross section exhibits a $E^{-1/2}$ dependence, again in agreement with the observations for many ion-molecule reactions.