

How do we monitor the progress of a reaction?

Monitor quantities that change during the reaction

If at least one component is a gas, we can monitor the change in pressure.

Example:



Let initial pressure = p_0

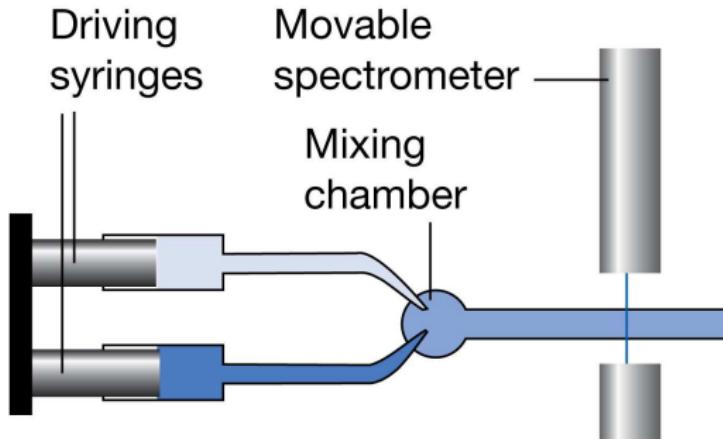
initial amount of $\text{N}_2\text{O}_5 = n$ mols

at time t , degree of dissociation = α

	N_2O_5	NO_2	O_2	total
amount	$n(1 - \alpha)$	$2\alpha n$	$\frac{1}{2}\alpha n$	$n\left(1 + \frac{3}{2}\alpha\right)$

When $\alpha = 0$, $p = p_0$ \therefore at time t , $p(t) = \left(1 + \frac{3}{2}\alpha\right) p_0$

real-time-analysis: flow technique



location of the spectrometer corresponds to different times after initiation

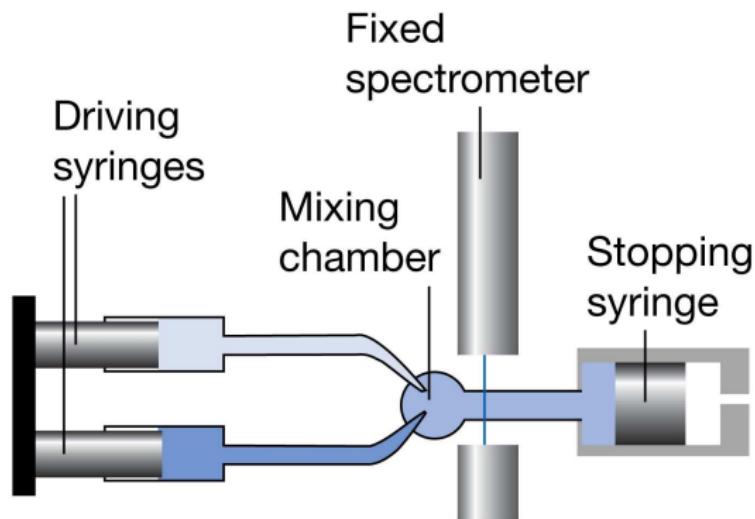
e.g., progress of the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

can be followed by measuring amount of visible light absorbed by $Br_2(g)$

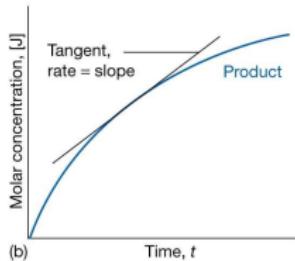
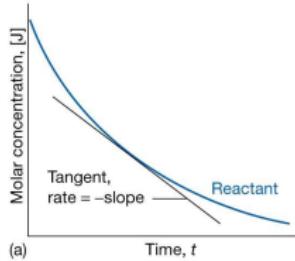
Similarly, changes in conductivity and pH can be used as means of monitoring the progress of a reaction

e.g., the reaction $(\text{CH}_3)_3\text{CCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow (\text{CH}_3)_3\text{COH}(\text{aq}) + \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
can be monitored by measuring either **conductivity** or **pH**

stopped-flow technique



instantaneous rate



$$\text{extent of reaction } \xi = \frac{n_J - n_{J,0}}{\nu_J}$$

J refers to species in a reaction mixture

n_J = amount of J at some time

$n_{J,0}$ = amount of J at initial time

ν_J = stoichiometric number of species J
 < 0 for reactants and > 0 for products

$$v = \frac{1}{V} \frac{d\xi}{dt}; V = \text{vol. of reaction mix.}$$

$$= \frac{1}{V} \frac{1}{\nu_J} \frac{dn_J}{dt}$$

$$\text{or, } v = \frac{1}{\nu_J} \frac{d[J]}{dt} \text{ (mol.dm}^{-3}\text{s}^{-1}\text{)}$$

for gas phase, (molecules.cm⁻³s⁻¹)

For a reaction $aA + bB \rightarrow cC + dD$, $v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \dots$

e.g., for $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, $v = -\frac{1}{2} \frac{d[\text{H}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{H}_2\text{O}]}{dt}$

For a heterogeneous reaction we use surface area, A , occupied by the species in place of V

and then use $\sigma_J = \frac{n_J}{A}$;

$$v = \frac{1}{\nu_J} \frac{d\sigma_J}{dt} \text{ (mol.m}^{-2}\text{s}^{-1}\text{)}$$

Rate laws, rate constants and reaction order :

Typical rate expression, $v = k [A]^m [B]^n$; k = rate constant

order w.r.t. $A = m \in \mathbb{R}$; order w.r.t. $B = n \in \mathbb{R}$; overall order = $m + n \in \mathbb{R}$

$v = f([A], [B], \dots)$: Rate law in terms of concentrations

$v = f(p_A, p_B, \dots)$: Rate law in terms of pressures

generally, $v = k \prod_{i=1}^N c_i^{n_i}$; n_i = order w.r.t. component i of N

an overall reaction may contain a set of elementary reactions

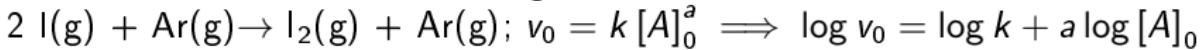
molecularity : # reactant molecules involved in an elementary step $\in \mathbb{Z}^+$

example : unimolecular, $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$

bimolecular, $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

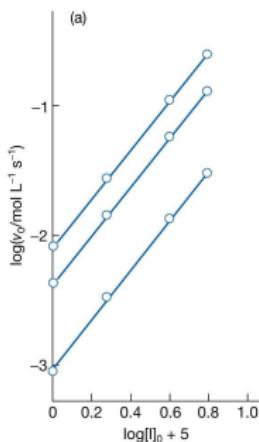
Method of initial rates:

Recombination of I atoms in the gas phase in the presence of Ar,

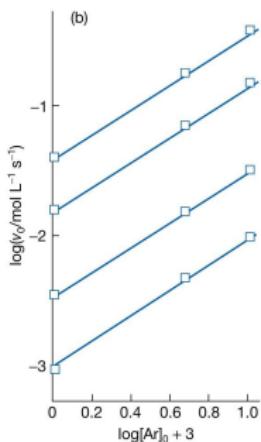


$[\text{I}]_0/(10^{-5} \text{ mol dm}^{-3})$	1.0	2.0	4.0	6.0
$v_0/(\text{mol dm}^{-3} \text{ s}^{-1})$	(a) 8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b) 4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c) 8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

$[\text{Ar}]$: (a) 1 mmol dm^{-3} (b) 5 mmol dm^{-3} and (c) 10 mmol dm^{-3}



$$\text{slope} = 2$$



$$\text{slope} = 1 \quad v_0 = k [\text{I}]_0^2 [\text{Ar}]_0$$

$$\text{intercept, } k = 9 \times 10^9 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

- ▶ method of initial rates might not reveal full rate law
- ▶ once products are generated they might participate in reaction and affect its rate
- ▶ e.g., products participate in the synthesis of HBr, $\text{H}_2 + \text{Br}_2 \rightarrow \text{HBr}$
 - ▶ full rate law depends on $[\text{HBr}]$
- ▶ To avoid this difficulty, rate law should be fitted to data throughout the reaction
- ▶ fitting may be done, in simple cases at least, by using a proposed rate law to predict concn. of any component at any time, and comparing it with data
- ▶ rate law should also be tested for whether
 - { addition of products
 - or, for gas phase, change in $\frac{\text{surface}}{\text{vol}}$ affects the rate

half-life

1st order reaction: $t_{\frac{1}{2}} = \frac{\ln 2}{k}$

time constant, $\tau = \frac{1}{k}$

integrated rate law: Zero- order rxn

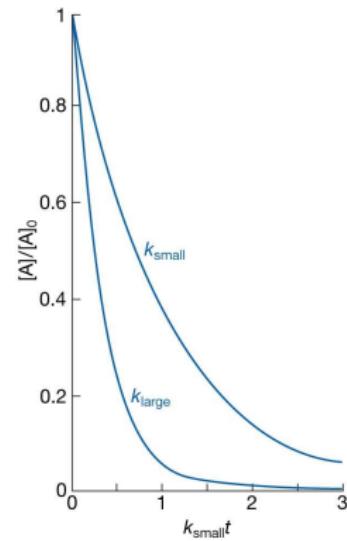
$$\frac{d[A]}{dt} = -k[A]^0 = -k$$

$$[A] = [A]_0 - kt$$

1st order rxn

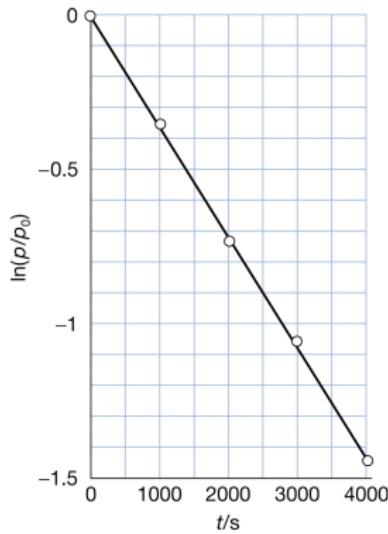
$$\frac{d[A]}{dt} = -k[A]$$

$$[A] = [A]_0 e^{-kt}$$





t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

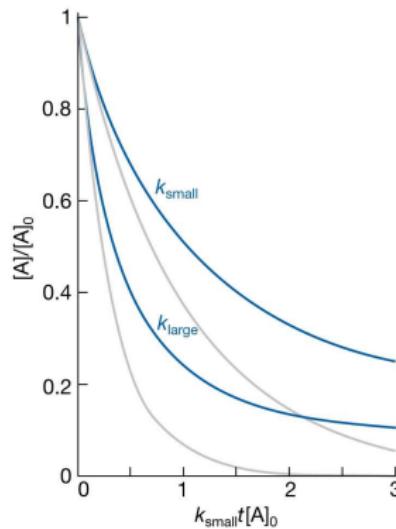


second-order:

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

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

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



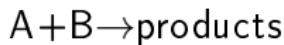
$$k_{\text{large}} = 3k_{\text{small}}$$

(grey lines for first order)

half life for second order reaction: $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$

In general, for n -th order reaction: $t_{\frac{1}{2}} = \frac{1}{k[A]_0^{n-1}}$

General second-order reaction:

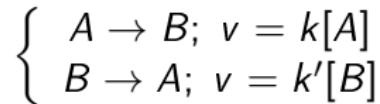


$$\frac{d[A]}{dt} = -k[A][B] = -k([A]_0 - x)([B]_0 - x) = -\frac{dx}{dt}$$

$$\ln \left(\frac{\frac{[B]}{[B]_0}}{\frac{[A]}{[A]_0}} \right) = ([B]_0 - [A]_0) kt$$

Order	Reaction	Rate law*
0	$A \rightarrow P$	$v = k_r$ $k_r t = x \text{ for } 0 \leq x \leq [A]_0$
1	$A \rightarrow P$	$v = k_r [A]$ $k_r t = \ln \frac{[A]_0}{[A]_0 - x}$
2	$A \rightarrow P$	$v = k_r [A]^2$ $k_r t = \frac{x}{[A]_0([A]_0 - x)}$
	$A + B \rightarrow P$	$v = k_r [A][B]$ $k_r t = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$
	$A + 2 B \rightarrow P$	$v = k_r [A][B]$ $k_r t = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$
	$A \rightarrow P$ with autocatalysis	$v = k_r [A][P]$ $k_r t = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$
3	$A + 2 B \rightarrow P$	$v = k_r [A][B]^2$ $k_r t = \frac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0}$ $+ \frac{1}{(2[A]_0 - [B]_0)^2} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$
$n \geq 2$	$A \rightarrow P$	$v = k_r [A]^n$

Reactions approaching equilibrium: $A \xrightleftharpoons[k']{k} B$



$$\begin{aligned} \frac{d[A]}{dt} &= -k[A] + k'[B] \\ &= -k[A] + k'([A]_0 - [A]) \\ &= -(k + k')[A] + k'[A]_0 \\ [A] &= \frac{k' + k e^{-(k+k')t}}{k + k'} [A]_0 \end{aligned}$$

Equilibrium: $t \rightarrow \infty$

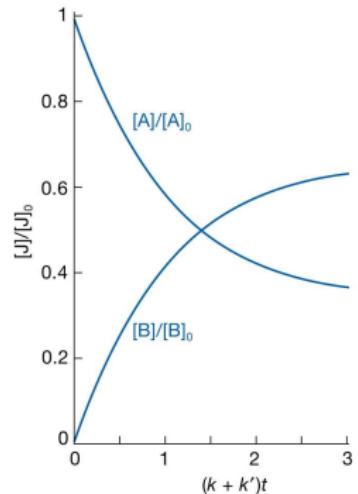
$$[A]_{eq} = \frac{k'[A]_0}{k+k'}; [B]_{eq} = \frac{k[A]_0}{k+k'}$$

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k}{k'} : \text{Principle of detailed balance}$$

theoretical importance: thermodynamics (K) \Leftrightarrow kinetics (k)

practical importance: $\{K, k, k'\}$ are related

more generally, $K = \frac{k_a}{k'_a} \cdot \frac{k_b}{k'_b} \cdot \frac{k_c}{k'_c} \cdots$



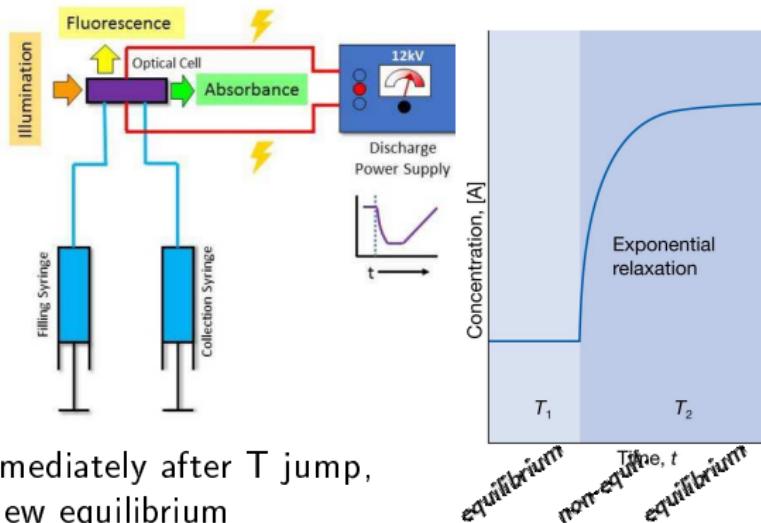
relaxation methods: temperature jump (Manfred Eigen, 1950s)

- method spanning $1 - 10^{-11}$ s time-scale

ΔT acts as a perturbation shifting the equilibrium; $\frac{\partial \ln K}{\partial T} = \frac{\Delta H^\ominus}{RT^2}$

: discharge a capacitor through a sample made conducting by the addition of ions
 $5 \leq \Delta T \leq 10$ K in $1\mu\text{s}$ with electrical discharges

45 J discharged in $1\mu\text{s}$ through 10 cc ; laser/MW discharges also used
pulsed lasers : $10 \leq \Delta T \leq 30$ K within nanoseconds in aq. samples



immediately after T jump,
new equilibrium

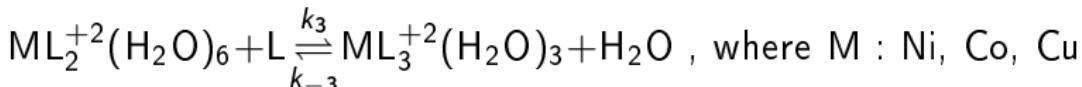
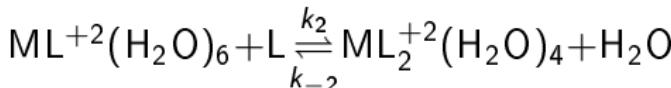
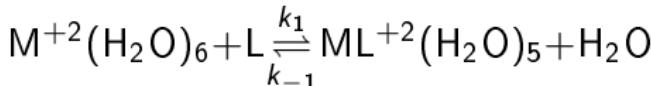
$$[A] = [A]_{\text{eq}} + x$$
$$[B] = [B]_{\text{eq}} - x$$

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

$$\text{show: } x = x_0 e^{-\frac{t}{\tau}}; \frac{1}{\tau} = k + k'$$
$$\tau = \text{relaxation constant}$$

Some equilibria are also sensitive to pressure :
pressure-jump techniques also used

Ex. : formation of transition-metal complexes

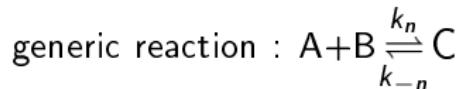
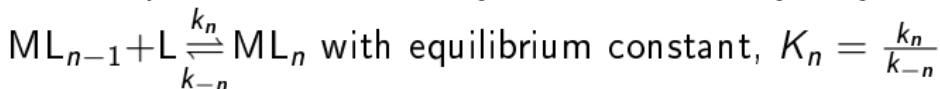


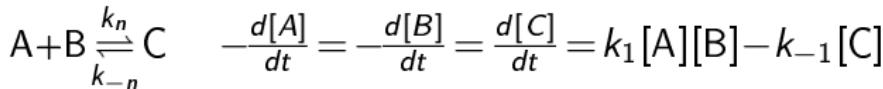
: : : and L : unidentate ligand, e.g. NH_3

- can be generalized to include charged ligands or multidentate ligands
like $NH_2(CH_2)NH_2$

when $[M^{+2}] \gg [L]$, the major species are M^{+2} and ML^{+2} . At higher concentrations of L, ML_2^{+2} and ML_3^{+2} may dominate.

For correct choice of initial concentrations,
the complex mechanism may be dominated by only one equilibrium,





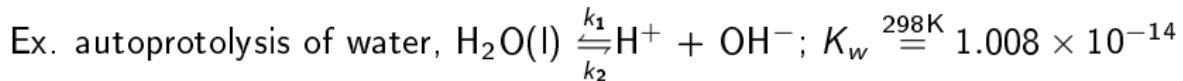
let a , b and c be new equilibrium concentrations after perturbing the system, and $-x = a - [A] = b - [B] = [C] - c$

$$\text{then } -\frac{d[A]}{dt} = -\frac{dx}{dt} = k_1(a + x)(b + x) - k_{-1}(c - x)$$

ignore second order terms, and use $k_1 ab = k_{-1} c$ and get,

$$\frac{dx}{dt} = -[k_1(a + b) + k_{-1}]x = -\frac{x}{\tau}$$

where τ = relaxation constant; and soln. : $x = x_0 e^{-\frac{t}{\tau}}$



After T-jump, equilibrium : $\tau_{\text{relaxation}} = 37\mu\text{s}$ at 298 K and $\text{pH} \approx 7$

Given : forward reaction is 1st-order and reverse 2nd- order overall
 calculate : rate constants for forward and reverse reactions

Ans. forward rate at final temp. $= k_1[\text{H}_2\text{O}]$; reverse rate $= k_2[\text{H}^+][\text{OH}^-]$

$$\text{net rate} = \frac{d[\text{H}_2\text{O}]}{dt} = -k_1[\text{H}_2\text{O}] + k_2[\text{H}^+][\text{OH}^-]$$

write $[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_{\text{eq}} + x$, $[\text{H}^+] = [\text{H}^+]_{\text{eq}} - x$ and $[\text{OH}^-] = [\text{OH}^-]_{\text{eq}} - x$

$$\frac{dx}{dt} = - \left\{ k_1 + k_2 \left([\text{H}^+]_{\text{eq}} + [\text{OH}^-]_{\text{eq}} \right) \right\} x - \underbrace{k_1 [\text{H}_2\text{O}]_{\text{eq}} + k_2 [\text{H}^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}}}_{=0} + \underbrace{k_2 x^2}_{\text{neglect}}$$

$$\therefore \frac{1}{\tau} = k_1 + k_2 \left([\text{H}^+]_{\text{eq}} + [\text{OH}^-]_{\text{eq}} \right) \text{ Also, } \frac{k_1}{k_2} = \frac{[\text{H}^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}}}{[\text{H}_2\text{O}]_{\text{eq}}}$$

$$\text{find } k_2 = 1.4 \times 10^{11} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ and } k_1 = 2.4 \times 10^{-5} \text{s}^{-1}$$

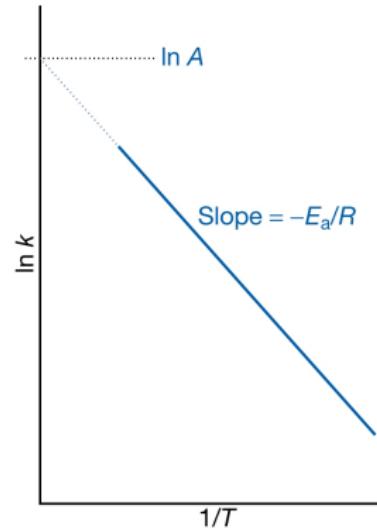
Temperature dependence of rate constant: Arrhenius behaviour

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

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

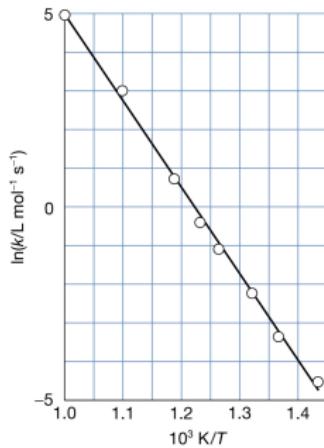
Activation energy:

$$E_a = RT^2 \left(\frac{d \ln k}{dT} \right)$$



second-order decomposition of acetaldehyde (ethanal, CH_3CHO)

T/K	700	730	760	790	810	840	910	1000
$k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145
$(10^3 \text{ K})/T$	1.43	1.37	1.32	1.27	1.23	1.19	1.10	1.00
$\ln(k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	-4.51	-3.35	-2.25	-1.07	-0.24	0.77	3.00	4.98



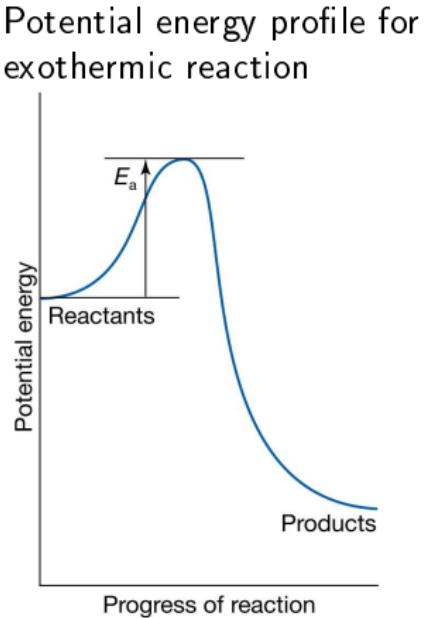
$$\text{slope} = -22.7$$

$$\text{intercept} = 27.7$$

$$\implies E_a = 22.7 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 10^3 \text{ K}$$

- stronger temperature dependence of rate constant (steeper slope)
 \Rightarrow higher activation energy
 - high activation energy
 \Rightarrow rate constant depends strongly on temperature.
 - zero activation energy \Rightarrow rate independent of temperature
 - negative activation energy \Rightarrow rate decreases as temperature is raised

$$E_a = RT^2 \left(\frac{d \ln k}{dT} \right)$$



activated complex
versus
transition state

Effect of catalyst

Consecutive elementary reactions: $A \xrightarrow{k_a} I \xrightarrow{k_b} P$

e.g., $^{239}\text{U} \xrightarrow{23.5 \text{ min}} ^{239}\text{Np} \xrightarrow{2.35 \text{ day}} ^{239}\text{Pu}$

$$\frac{d[A]}{dt} = -k_a[A] \dots \dots \dots (1)$$

$$\frac{d[I]}{dt} = k_a[A] - k_b[I] \dots \dots \dots (2)$$

$$\frac{d[P]}{dt} = k_b[I] \dots \dots \dots (3)$$

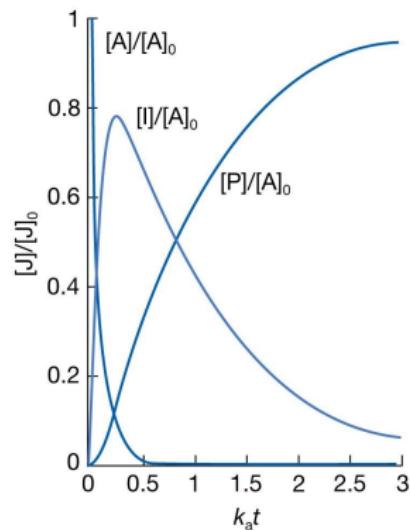
$$[A] + [I] + [P] = [A]_0 \dots \dots \dots (4)$$

$$(1) \implies [A] = [A]_0 e^{-k_a t} \dots \dots \dots (5)$$

(2) & (5)

$$\implies \frac{d[I]}{dt} + k_b[I] = k_a[A]_0 e^{-k_a t} \dots \dots \dots (6)$$

$$\implies [I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) [A]_0$$



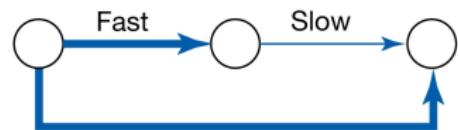
$$k_a = 10k_b$$



(a)

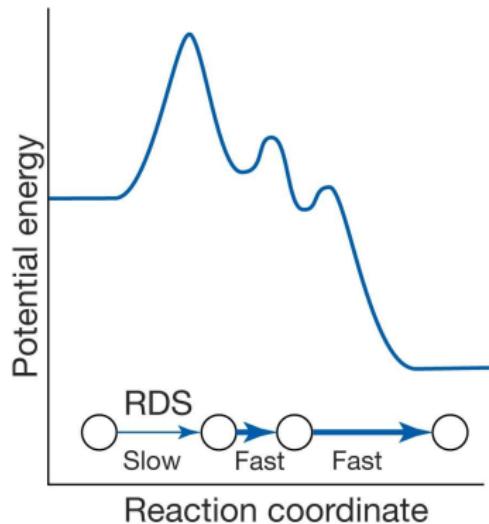


(b)



(c)

slow step is rate determining [not in (c)]



steady state approximation: $\frac{d[I]}{dt} = 0$

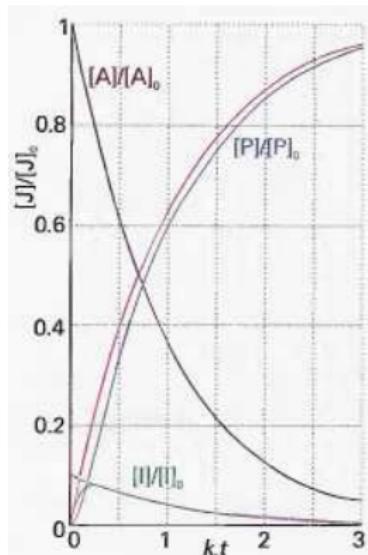
$$\begin{aligned}\frac{d[I]}{dt} &= k_a[A] - k_b[I] = 0 \\ \Rightarrow [I] &= \left(\frac{k_a}{k_b}\right) [A]\end{aligned}$$

The concentrations of the intermediates remains small and hardly changes during reaction.

$$\Rightarrow \frac{k_a}{k_b} \ll 1$$

$$\Rightarrow \frac{d[P]}{dt} = k_b[I] = k_a[A] = [A]_0 e^{-k_a t}$$

$$\Rightarrow [P] = [A]_0 \int_0^t e^{-k_a t} = (1 - e^{-k_a t}) [A]_0$$



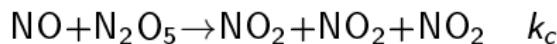
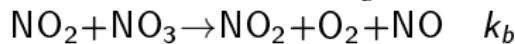
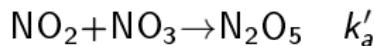
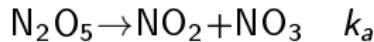
$$k_b = 20k_a$$

exact (black) versus s.s. (red)

example: decomposition of N_2O_5 :



given mechanism:



rate law?

Identified intermediates: NO and NO_3

$$\begin{aligned}\frac{d[\text{NO}]}{dt} &= k_b[\text{NO}_2][\text{NO}_3] - k_c[\text{NO}][\text{N}_2\text{O}_5] = 0 \\ \implies k_c[\text{NO}][\text{N}_2\text{O}_5] &= k_b[\text{NO}_2][\text{NO}_3]\end{aligned}$$

$$\begin{aligned}\frac{d[\text{NO}_3]}{dt} &= k_a[\text{N}_2\text{O}_5] - k'_a[\text{NO}_2][\text{NO}_3] - k_b[\text{NO}_2][\text{NO}_3] = 0 \\ \implies [\text{NO}_2][\text{NO}_3] &= \frac{k_a[\text{N}_2\text{O}_5]}{k'_a + k_b}\end{aligned}$$

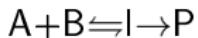
and the rate of decomposition of N_2O_5 :

$$\begin{aligned}\frac{d[\text{N}_2\text{O}_5]}{dt} &= -k_a[\text{N}_2\text{O}_5] + k'_a[\text{NO}_2][\text{NO}_3] - k_c[\text{NO}][\text{N}_2\text{O}_5] \\ &= -k_a[\text{N}_2\text{O}_5] + k'_a \frac{k_a[\text{N}_2\text{O}_5]}{k'_a + k_b} - k_b \frac{k_a[\text{N}_2\text{O}_5]}{k'_a + k_b} = -\frac{2k_a k_b [\text{N}_2\text{O}_5]}{k'_a + k_b}\end{aligned}$$

Kinetic and thermodynamic control

When rate of decay of intermediate back into reactants much faster than rate of product formation ($k'_a \gg k_b$)

Pre-equilibria:



$$K = \frac{[I]}{[A][B]} = \frac{k_a}{k'_a}$$

$$\text{rate law: } \frac{d[P]}{dt} = k_b[I] = k_b K[A][B];$$

second order

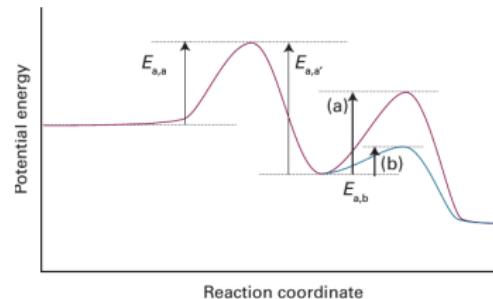
$$\text{composite rate constant} = k_b K = \frac{k_a k_b}{k'_a}$$

3 activation energies to take into account:

two referring to reversible steps of pre-equilibrium and one for final step

relative magnitudes of activation energies determine

overall activation energy (a) > 0 or (b) < 0



If we include the details:

$$\frac{d[I]}{dt} = k_a[A][B] - k'_a[I] - k_b[I] = 0$$

then $[I] = \frac{k_a[A][B]}{k'_a + k_b}$

and $\frac{d[P]}{dt} = k_b[I] = k[A][B]; \quad k = \frac{k_a k_b}{k'_a + k_b}$

same as before for $k'_a \gg k_b$

kinetic isotope effect : decrease in rate on replacing an atom in reactant by heavier isotope

primary : rate-determining step requires scission of bond involving the isotope.

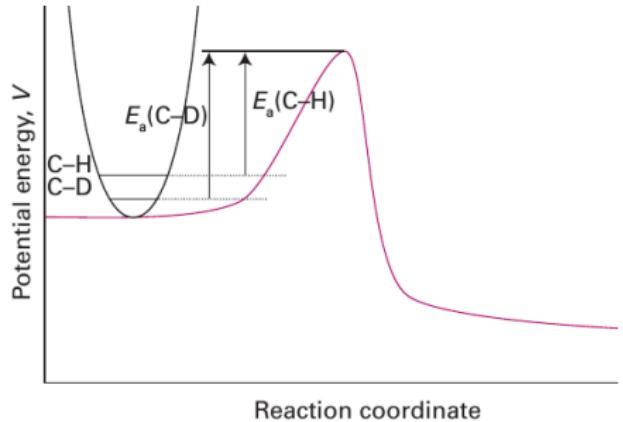
secondary : bond involving isotope not broken from product

$$\Delta E_a = E_{C-D} - E_{C-H}$$

$$= \frac{1}{2} \hbar \omega_{C-H} \left[1 - \sqrt{\left(\frac{\mu_{CH}}{\mu_{CD}} \right)} \right]$$

$$\frac{k_D}{k_H} = e^{-\lambda}; \quad \lambda = \frac{\Delta E_a}{k_b T} > 0$$

$\therefore \frac{k_D}{k_H}$ decreases with decreasing temperature



Secondary kinetic effect: arises from differences in zero-point energies between reactants and activated complex with significantly different structure

undeuterated:

$$E_{a(H)} = E_a + E_{\text{vib},0(H)}^\dagger - E_{\text{vib},0(H)}$$

deuterated:

$$E_{a(D)} = E_a + E_{\text{vib},0(D)}^\dagger - E_{\text{vib},0(D)}$$

$$E_{a(D)} - E_{a(H)} =$$

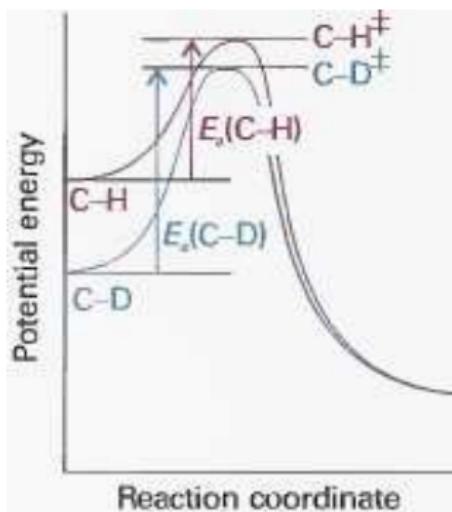
$$\left\{ E_{\text{vib},0(\text{D})}^{\ddagger} - E_{\text{vib},0(\text{D})} \right\}$$

$$- \left\{ E_{\text{vib},0(\mathbf{H})}^{\ddagger} - E_{\text{vib},0(\mathbf{H})} \right\}$$

$$= \frac{1}{2} N_A h c \left[\left\{ \bar{\nu}_D^{\ddagger} - \bar{\nu}_D \right\} - \left\{ \bar{\nu}_H^{\ddagger} - \bar{\nu}_H \right\} \right]$$

$$= \frac{1}{2} N_A h c \left\{ \bar{\nu}_H - \bar{\nu}_H^\dagger \right\} \left\{ 1 - \sqrt{\frac{\mu_{CH}}{\mu_{CD}}} \right\}$$

$$\frac{k_D}{k_H} = e^{-\lambda}; \quad \lambda = \frac{\Delta E_a}{k_b T} > 0$$



Comparison $\bar{\nu}_{C-H} = 3000 \text{ cm}^{-1}$; $\frac{\mu_{CH}}{\mu_{CD}} = 0.538$;

$$\Delta E_a = \frac{1}{2}hc \times 3000 [1 - \sqrt{0.538}]$$

Primary kinetic effect: $\frac{k_D}{k_H} = e^{-\frac{\Delta E_a}{k_b T}} = 0.145$

Secondary kinetic effect:



activated complex resembles product CHCl_2^+ .

for bending motion involving C-H group

$$\bar{\nu} = \begin{cases} 1350 \text{ cm}^{-1} \text{ in } \text{CHCl}_3 \\ 800 \text{ cm}^{-1} \text{ in } \text{CHCl}_2^+ \approx \bar{\nu}^\ddagger \end{cases} \quad \Delta E_a = \frac{1}{2}hc (1350 - 800) [1 - \sqrt{0.538}]$$

$$\frac{k_D}{k_H} = e^{-\frac{\Delta E_a}{k_b T}} = 0.709$$

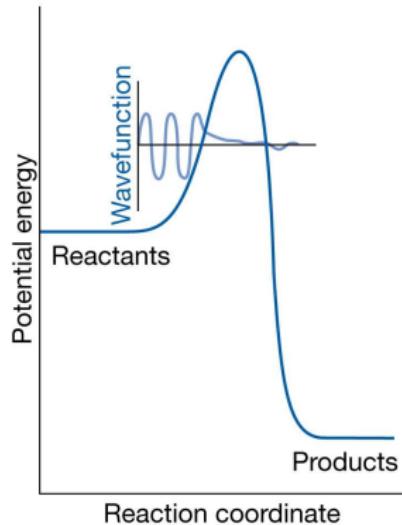
secondary kinetic isotope effect : higher values of $\frac{k_D}{k_H}$ than primary effect
conclusion supported by a number of experimental observations

tunneling: reduction of effective barrier height

In some cases, substitution of D for H results in values of $\frac{k_D}{k_H}$ too low

Such abnormal effects are evidence of quantum mechanical tunnelling of H atoms through activation barrier

probability of tunnelling through a barrier decreases as mass of particle increases, so D tunnels less efficiently than H and its reactions are slower



unimolecular process, $A^* \rightarrow P$:

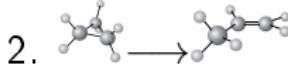
* : A contains sufficient vibrational energy to decompose

Three general types of PE profile

isomerization



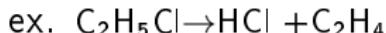
substantial barrier



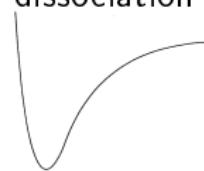
dissociation



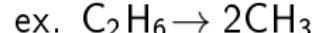
large E_a in both forward and reverse direction



dissociation

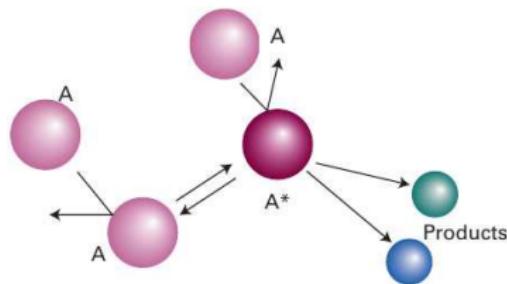
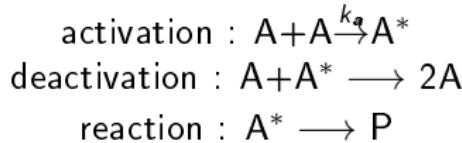


no E_a for reverse reaction



Lindemann-Hinshelwood mechanism

Assumpn. : reactant molecule A becomes energetically excited by collision with another molecule in a bimolecular step





$$\frac{d[A^*]}{dt} = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*] = 0 \text{ (s.s.)}$$

$$\Rightarrow [A^*] = \frac{k_a[A]^2}{k_b + k'_a[A]}$$

If rate of deactivation by collisions \gg rate of decay to products,

i. e., $k'_a[A][A^*] \gg k_b[A^*]$, or, $k'_a[A] \gg k_b$

then $\frac{d[P]}{dt} = k_b[A^*] = k[A]$; $k = \frac{k_a k_b}{k'_a}$: 1st order

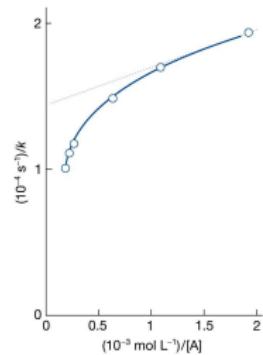
if $[A]$ is reduced, $k'_a[A] \ll k_b$

then $\frac{d[P]}{dt} = k[A]$; $k = k_a[A]^2$: 2nd order

generally, equating the empirical and theoretical expressions,

$$\text{rate} = k[A] = k_b[A^*] = \frac{k_b k_a [A]^2}{k_b + k'_a [A]}$$

$$\text{or, } \frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a [A]}$$



unimolecular isomerization of trans-CHD=CHD shows departure from straight line predicted by L-H mechanism

RRKM model: A molecule may have enough energy to react, that energy is distributed over all modes of motion reaction will occur only when enough of that energy has migrated into reactive mode.

How do we distribute n quanta of energy in different modes?

For vibrational modes, the quanta follow Bose-Einstein statistics:

n balls (quanta of energy) to be arranged in s containers (energy states)

$$\# \text{ ways, } N = \frac{(n+s-1)!}{n!(s-1)!}$$

Energy is too sparsely spread over all modes for a particular bond to be sufficiently highly excited to undergo dissociation.

Suppose a bond breaks if it is excited to at least an energy $E^* = n^* h\nu$, then $\#$ ways in which this energy can be localized in one bond

$$N^* = \frac{(n-n^*+s-1)!}{(n-n^*)!(s-1)!}$$

Probability that a specific oscillator has sufficient excitation to dissociate,

$$P = \frac{N^*}{N} = \frac{n!(n-n^*+s-1)!}{(n-n^*)!(n+s-1)!}$$

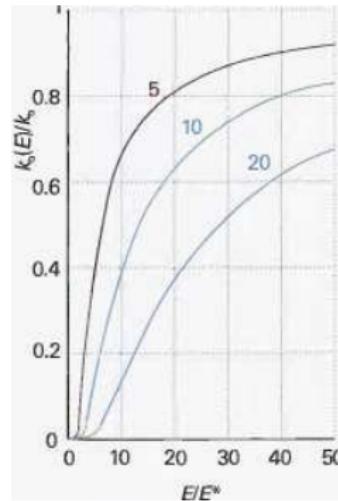
For $s-1 \ll n-n^*$

$$P \approx \frac{n!(n-n^*)^{s-1}(n-n^*)!}{(n-n^*)!n^{s-1}.n!} = \left(\frac{n-n^*}{n}\right)^{s-1} = \left(1 - \frac{E^*}{E}\right)^{s-1}$$

Dispersal of collision energy reduces rate constant below its simple 'Lindemann' form,

To obtain observed rate constant we should multiply the Lindemann result by the probability that energy will in fact be localized in a bond of interest

$$k_b(E) = k_b \left(1 - \frac{E^*}{E}\right)^{s-1} \text{ for } E \geq E^*$$



Energy dependence of rate constant for three values of s

Rate of each step of a complex mechanism increases with temp

is that true of a composite reaction?

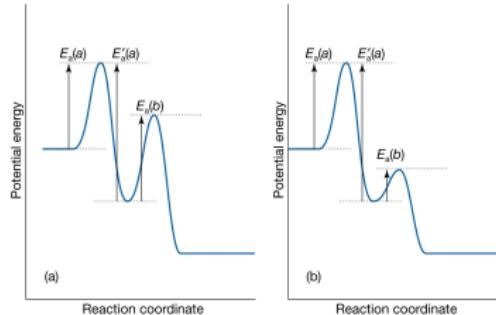
consider the high-pressure limit of the L-H mechanism

$$k = \frac{k_a k_b}{k'_a} = \frac{\left(A_a e^{-\frac{E_a}{RT}}\right) \left(A_b e^{-\frac{E_b}{RT}}\right)}{\left(A_{a'} e^{-\frac{E_{a'}}{RT}}\right)} = \frac{A_a A_b}{A_{a'}} e^{-\frac{E_a + E_b - E_{a'}}{RT}}$$

If $E_a + E_b > E_{a'}$, then rate increases with temp

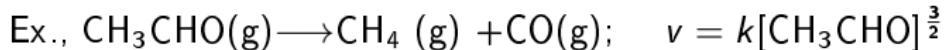
If $E_a + E_b < E_{a'}$, then rate decreases with temperature

reaction with a pre-equilibrium: 3 activation energies to take into account

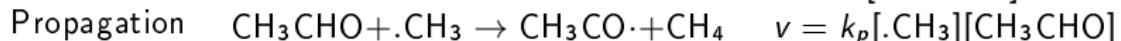


There are reactions in which negative activation energy is observed

Chain reaction:



Rice-Herzfeld mechanism:



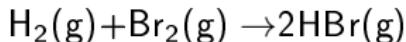
$$\text{SSA : } \frac{d[\cdot\text{CH}_3]}{dt} = k_i[\text{CH}_3\text{CHO}] - k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k'_p[\text{CH}_3\text{CO}\cdot] - 2k_t[\cdot\text{CH}_3]^2 = 0$$
$$\frac{d[\text{CH}_3\text{CO}\cdot]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k'_p[\text{CH}_3\text{CO}\cdot] = 0$$

Add and get: $k_i[\text{CH}_3\text{CHO}] = 2k_t[\cdot\text{CH}_3]^2 \Rightarrow$

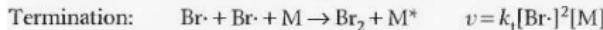
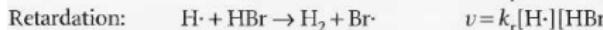
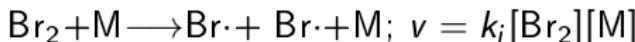
\Rightarrow rate of initiation = rate of termination

$$\text{rate of reaction} = \frac{d[\text{CH}_4]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] = k_p \sqrt{\frac{k_i}{2k_t}} [\text{CH}_3\text{CHO}]^{\frac{3}{2}}$$

mechanism does not explain other by-products like propanone and propanal



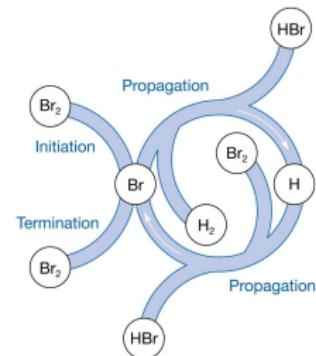
Initiation:



M is either Br_2 or H_2 .

net rate:

$$\frac{d[HBr]}{dt} = k_p [Br][H_2] + k'_p [H][Br_2] - k_r [H][HBr] - k_t [Br]^2 [M]$$



$$\text{ss: } \frac{d[H]}{dt} = k_p[Br][H_2] - k_{p'}[H][Br_2] - k_r[H][HBr] = 0$$

$$\frac{d[Br]}{dt} = 2k_i[Br_2][M] - k_p[Br][H_2] + k_{p'}[H][Br_2] + k_r[H][HBr] - 2k_t[Br]^2[M] = 0$$

$$\text{Adding, } 2k_i[Br_2][M] = 2k_t[Br]^2[M], \text{ or, } [Br] = \sqrt{\frac{k_i}{k_t}}[Br_2]^{\frac{1}{2}}$$

Using this in first equation:

$$k_{p'}[H][Br_2] + k_r[H][HBr] = k_p[Br][H_2] = k_p \sqrt{\frac{k_i}{k_t}} [Br_2]^{\frac{1}{2}} [H_2]$$

$$\Rightarrow [H] = \frac{k_p \sqrt{\frac{k_i}{k_t}} [H_2][Br_2]^{\frac{1}{2}}}{k_{p'}[Br_2] + k_r[HBr]}$$

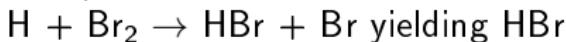
$$\text{using } k_{p'}[H][Br_2] = k_p[Br][H_2] - k_r[H][HBr]$$

$$\therefore \text{net rate: } \frac{d[HBr]}{dt} = 2k_{p'}[H][Br_2]$$

$$= \frac{2k_p \sqrt{\frac{k_i}{k_t}} [H_2][Br_2]^{\frac{3}{2}}}{[Br_2] + \frac{k_r}{k_{p'}} [HBr]} = \frac{k[H_2][Br_2]^{\frac{3}{2}}}{[Br_2] + k'[HBr]}$$

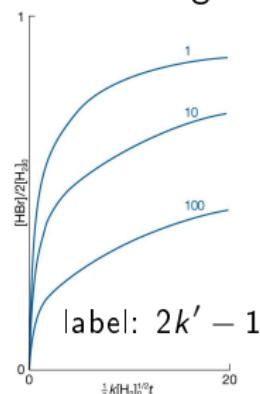
Reaction slows down as HBr forms, $\frac{[HBr]}{[Br_2]}$ increases \Leftarrow

Br₂ competes with HBr for H atoms, with propagation



retardation H + HBr \rightarrow H₂ + Br converts HBr back to H₂

numerical integrn :

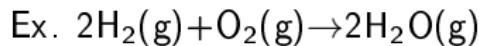


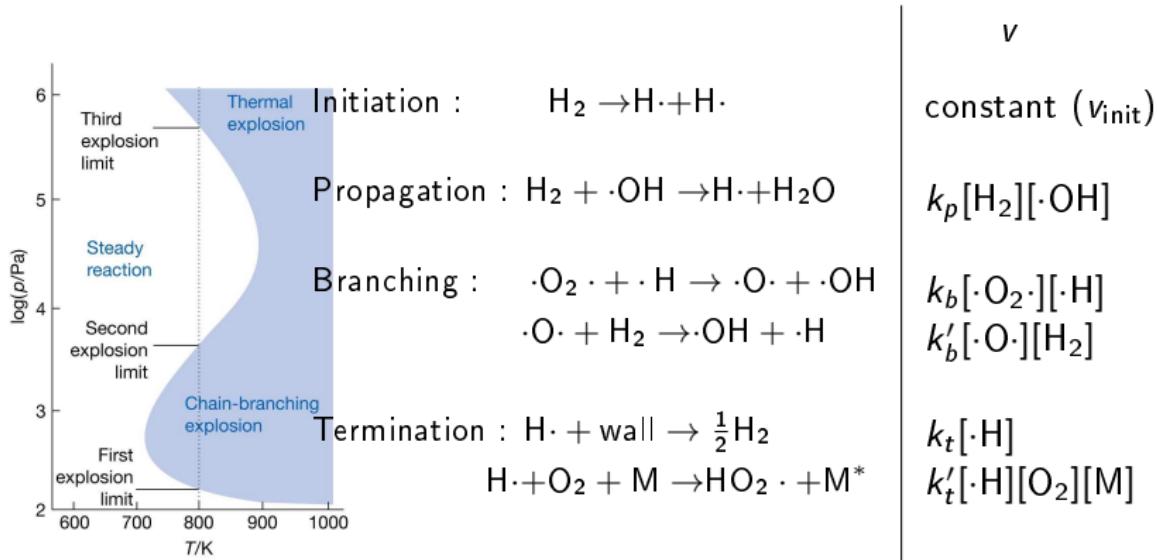
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Explosions:

rapid increase in reaction rate with increasing temp

if $\Delta_r H < 0$ and heat does not escape, reaction goes faster





branching step :

elementary reaction producing more than one chain carrier

$H_2 \rightarrow H\cdot + H\cdot$	constant (v_{init})
$H_2 + \cdot OH \rightarrow H\cdot + H_2O$	$k_p[H_2][\cdot OH]$
$\cdot O_2 \cdot + \cdot H \rightarrow \cdot O\cdot + \cdot OH$	$k_b[\cdot O_2\cdot][\cdot H]$
$\cdot O\cdot + H_2 \rightarrow \cdot OH + \cdot H$	$k'_b[\cdot O\cdot][H_2]$
$H\cdot + \text{wall} \rightarrow \frac{1}{2}H_2$	$k_t[\cdot H]$
$H\cdot + O_2 + M \rightarrow HO_2\cdot + M^*$	$k'_t[\cdot H][O_2][M]$

rate of formation of $H\cdot$ radical, $v_{rad} \equiv \frac{d[H]}{dt}$

$$v_{rad} = v_{init} + k_p[OH][H_2] - k_b[O_2][H] + k'_b[O][H_2] - k_t[H] - k'_t[H][O_2][M]$$

$$\text{SS: } \frac{d[O]}{dt} = k_b[O_2][H] - k'_b[O][H_2] = 0 \implies [O] = \frac{k_b[O_2][H]}{k'_b[H_2]}$$

$$\frac{d[OH]}{dt} = -k_p[OH][H_2] + k_b[O_2][H] + k'_b[O][H_2] = 0$$

$$\text{or, } k_p[OH][H_2] = 2k_b[O_2][H] \implies [OH] = \frac{2k_b[O_2][H]}{k_p[H_2]}$$

$$\begin{aligned} \therefore v_{rad} &= v_{init} + 2k_b[O_2][H] - \cancel{k_b[O_2][H]} + \cancel{k_b[O_2][H]} - k_t[H] - k'_t[H][O_2][M] \\ &= v_{init} + (2k_b[O_2] - k_t - k'_t[O_2][M])[H] = v_{init} + (k_{branch} - k_{term})[H] \end{aligned}$$

$$v_{\text{rad}} = v_{\text{init}} + (k_{\text{branch}} - k_{\text{term}})[\text{H}], \quad \text{or, } \frac{d[\text{H}]}{dt} = v_{\text{init}} - (k_{\text{term}} - k_{\text{branch}})[\text{H}]$$

[O₂]

low : $k_{term} > k_{branch}$

high : $k_{branch} > k_{term}$

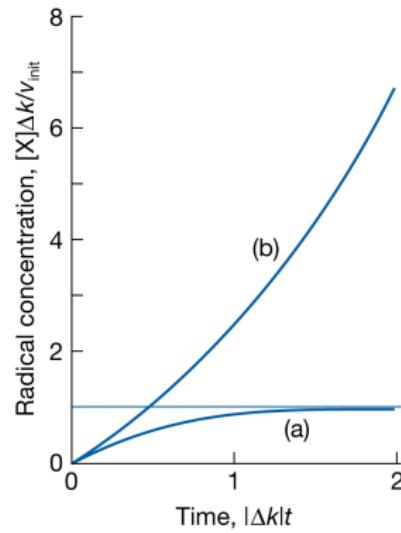
$$k_{\text{term}} = k_{\text{branch}}$$

[H]

$$\frac{v_{init}}{k_{term} - k_{branch}} (1 - e^{-(k_{term} - k_{branch})t}) \quad \text{steady combustion (a)}$$

$$\frac{v_{init}}{k_{branch} - k_{term}} (e^{(k_{branch} - k_{term})t} - 1) \quad \text{explosion (b)}$$

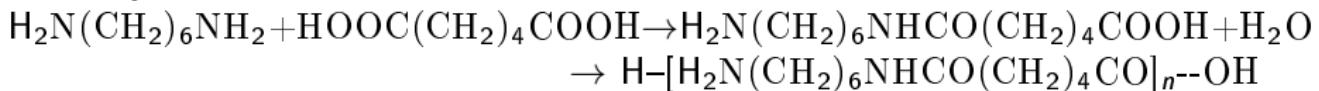
$v_{init} t$



stepwise polymerisation:

condensation reaction:

ex. Nylon-66



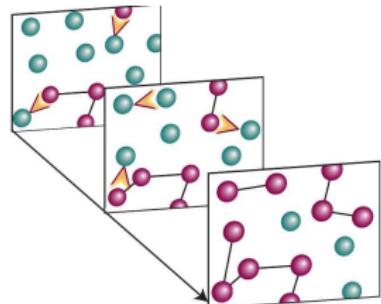
other ex.: polyesters, polyurethanes, etc.

monomers present can link together any time

growth not confined to chains already forming

monomers removed early

average molar mass increases in time





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

assume: rate constant independent of chain length
then k remains constant

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

fraction of A groups that have condensed at time t ,

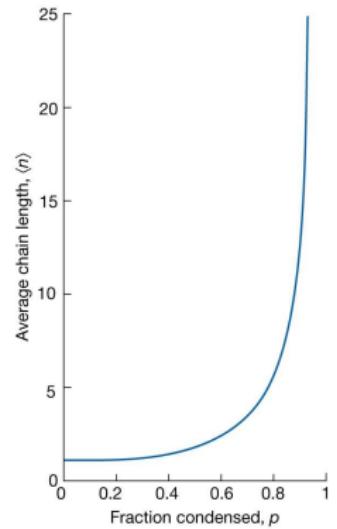
$$p = \frac{[A]_0 - [A]}{[A]_0} = \frac{kt[A]_0}{1+kt[A]_0}$$

degree of polymerisation: average # monomer residues per polymer molecule

$$\langle n \rangle = \frac{[A]_0}{[A]} = \frac{1}{1-p} = 1 + kt[A]_0$$

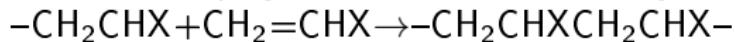
average length grows linearly in time

∴ longer a stepwise polymerisation proceeds, higher the average molar mass of product

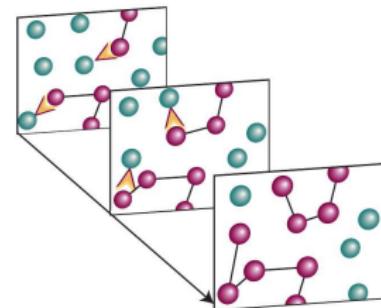


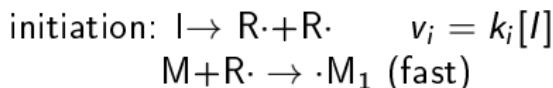
Chain polymerisation: addition of monomers to a growing polymer

Ex. addition polymerisation of ethene, methyl methacrylate, styrene, etc.

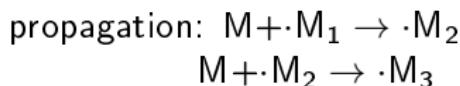


$$\text{rate, } v = k\sqrt{[I][M]}; \quad I \equiv \text{initiator}$$





sometimes the initiation leads to ionic chain carrier



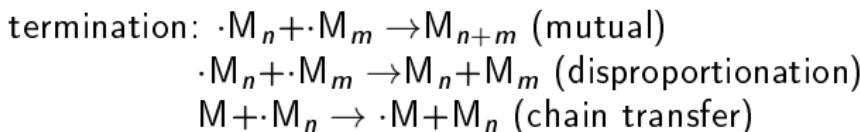
⋮



If rate of propagation independent of chain size, then
for large chains, rate of propagation = rate of polymerisation

rate of growth of radical concentration, $\left(\frac{d[\cdot M]}{dt} \right)_{\text{production}}$
= rate determining initiation rate, $2fk_i[I]$

where f = fraction of radicals that initiate a chain



Assume only mutual termination; $v_t = k_t[\cdot M]^2$

for every step, two radicals disappear,

$$\therefore \left(\frac{d[\cdot M]}{dt} \right)_{\text{depletion}} = -2k_t[\cdot M]^2$$

$$\text{SS: } \frac{d[\cdot M]}{dt} = 2fk_i[I] - 2k_t[\cdot M]^2 = 0 \implies [\cdot M] = \sqrt{\frac{fk_i}{k_t}}[I]^{\frac{1}{2}}$$

rate of propagation = - rate at which the monomer is consumed,

$$\therefore v_p = -d[M]/dt = k_p[M][\cdot M] = k_p \sqrt{\frac{fk_i}{k_t}} [I]^{\frac{1}{2}} [M] = \text{rate of polymerisation.}$$

kinetic chain length, $\nu = \frac{\text{\# monomers consumed}}{\text{\# activated centers produced}} = \frac{\text{rate of propagation of chains}}{\text{rate of production of radicals}}$

ss: rate of production of radicals = termination rate

$$\therefore \nu = \frac{k_p[M][\cdot M]}{2k_t[\cdot M]^2} = \frac{k_p[M]}{2k_t[\cdot M]} = k[M][I]^{-\frac{1}{2}}; \quad k = \frac{1}{2} \frac{k_p}{\sqrt{fk_i k_t}}$$

For mutual termination, $\langle n \rangle = \nu + \nu = 2\nu = 2k[M][I]^{-\frac{1}{2}}$

\therefore slower initiation \implies greater chain length \equiv higher average molar mass

catalysis:

decomposition of H_2O_2 in solution,

$E_{\text{act}} = 76 \text{ kJ mol}^{-1}$ at 298K.

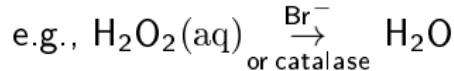
When a little I^- ion is added, $E_{\text{act}} = 57 \text{ kJ mol}^{-1}$

k increases by a factor of 2000

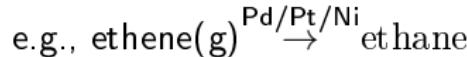
With Enzyme catalase $E_{\text{act}} = 8 \text{ kJ mol}^{-1}$

k increases by a factor of 10^{15}

Homogeneous : catalyst in same phase as reaction mixture

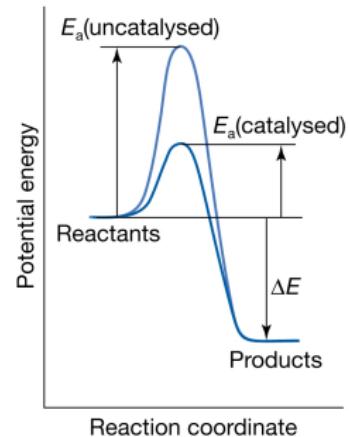


Heterogeneous : catalyst in different phase as reaction mixture,



metal provides surface upon which reactants bind

binding facilitates encounters between reactants and increases rxn rate



Catalysis and equilibrium

Effect of catalyst C on a slow reaction $A \rightarrow B$: $A + C \rightarrow B + C$

If overall reversible : $A \xrightleftharpoons[k_{-1}]{k_1} B$ with $\frac{k_1}{k_{-1}} = K_{\text{eq}} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}}$

then catalysed path : $A + C \xrightleftharpoons[k_{-2}]{k_2} B + C$ with $\frac{k_2}{k_{-2}} = K'_{\text{eq}} = \frac{[B]_{\text{eq}}[C]_{\text{eq}}}{[A]_{\text{eq}}[C]_{\text{eq}}} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = K_{\text{eq}}$

eq. const. for catalysed path = eq. const. for uncatalysed path

forward rate coeff. k_1 must be accelerated by exactly same factor

as reverse rate coeff. k_{-1}

Homogeneous catalysis - catalyst uniformly dispersed in reaction mixture:

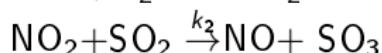
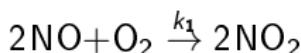
Consider a) Important industrial process for production of H_2SO_4 : $2\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$

$$\Delta_r G_{300\text{K}}^\ominus = -196 \text{ kJ/mol} \implies K_{\text{eq}} = 2.3 \times 10^{34} \text{ for reactants in standard states}$$

But SO_2 and O_2 are stable at room temp.

To carry out the reaction, a solid catalyst containing vanadium is most widely used

In gas phase, NO can be used



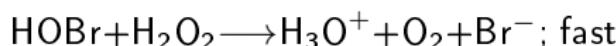
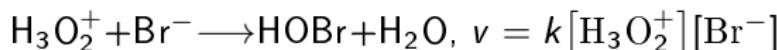
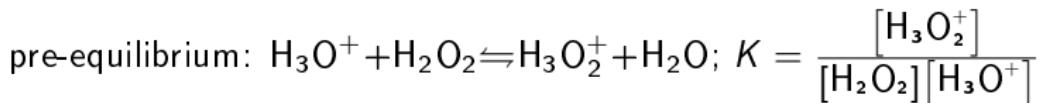
At high temp., second reaction is much faster than the first

$$\text{SSA : } \frac{d[\text{NO}]}{dt} = 0 \text{ (necessary for catalyst) and } \frac{d[\text{NO}_2]}{dt} = 0 \implies 2k_1[\text{NO}]^2[\text{O}_2] = k_2[\text{NO}]_2[\text{SO}_2]$$

$$\therefore \text{rate of formation of } \text{SO}_3: \frac{d[\text{SO}_3]}{dt} = k_2[\text{NO}_2][\text{SO}_2] = 2k_1[\text{NO}]^2[\text{O}_2]$$

Notice : No $[\text{SO}_2]$ appears in rate of formation of $[\text{SO}_3]$

b) Br^- -catalysed decomposition of H_2O_2 : $2\text{H}_2\text{O}_2(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

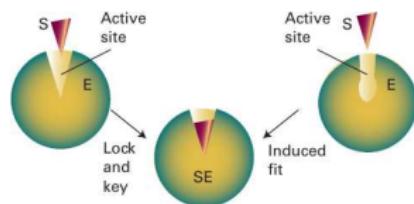


Experimentally variation of rate with $[\text{Br}^-]$ and pH agrees with above

Other examples: Acid/base catalysis

Enzyme catalysis (Homogeneous)

lock-n-key: active site and substrate have complementary 3D structures



induced fit model: binding induces a conformational change in active site

active site returns to its original state after products are released

Many enzymes consist primarily of proteins
some featuring organic or inorganic co-factors in active sites

Certain RNA molecules can also be biological catalysts, forming ribozymes
example of ribozyme \Rightarrow ribosome, large assembly of proteins and
catalytically active RNA molecules responsible for synthesis of proteins in cell

1. For a given initial concentration of substrate, $[S]_0$,
initial rate of product formation \propto total concentration of enzyme, $[E]_0$
2. For a given $[E]_0$ and low values of $[S]_0$,

rate of product formation $\propto [S]_0$.

3. For a given $[E]_0$ and high values of $[S]_0$,
rate of product formation : independent of $[S]_0$
reaches maximum velocity, v_{\max}

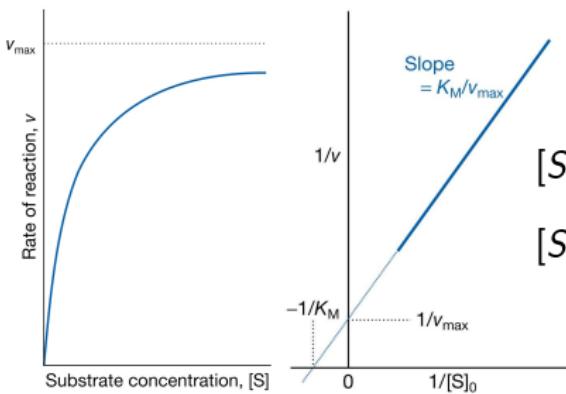
Michaelis-Menten mechanism: $E + S \xrightleftharpoons[k_a]{k_a'} ES \xrightarrow{k_b} P + E$;

$$SSA \implies \frac{d[ES]}{dt} = k_a [E][S] - k_a' [ES] - k_b [ES] = 0$$

$$\text{or, } [ES] = \frac{k_a}{k_a' + k_b} [E][S] = K_M^{-1} [E][S]$$

$$\text{Using } [E] = [E]_0 - [ES]; \quad K_M [ES] = ([E]_0 - [ES]) [S]$$

$$\text{or, } (K_M + [S]) [ES] = [E]_0 [S] \implies [ES] = \frac{[E]_0}{1 + \frac{K_M}{[S]}} \approx \frac{[E]_0}{1 + \frac{K_M}{[S]_0}}$$



$$\text{Slope} = K_M/v_{\max}$$

$$v = \frac{v_{\max}}{1 + \frac{K_M}{[S]_0}}; \quad v_{\max} = k_b [E]_0$$

$$[S]_0 \ll K_M \implies v = \frac{k_b}{k_M} [S]_0 [E]_0$$

$$[S]_0 \gg K_M \implies v = v_{\max} = k_b [E]_0$$

$$\frac{1}{v} = \frac{1}{v_{\max}} + \left(\frac{K_M}{v_{\max}} \right) \frac{1}{[S]_0}$$

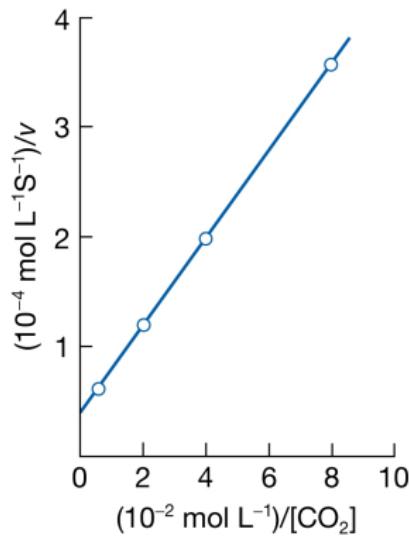
Lineweaver-Burk plot

Lineweaver-Burk plot

catalysis of hydration of CO_2 in red blood cells by carbonic anhydrase

$[\text{CO}_2]/(\text{mmol dm}^{-3})$	1.25	2.5	5	20
rate/(\text{mmol dm}^{-3} \text{s}^{-1})	2.78×10^{-2}	5.00×10^{-2}	8.33×10^{-2}	1.67×10^{-1}
$1/([\text{CO}_2]/(\text{mmol dm}^{-3}))$	0.800	0.400	0.200	0.0500
$1/(v/(\text{mmol dm}^{-3} \text{s}^{-1}))$	36.0	20.0	12.0	6.0

and $[E]_0 = 2.3 \times 10^{-9} \text{ mol} \cdot \text{dm}^{-3}$



$$v_{\max} = \frac{1}{0.4 \times 10^4} \text{ mol} \cdot \text{dm}^{-3} \text{s}^{-1}$$

$$= \frac{10^3}{4 \times 10^3} = 0.25 \text{ mmol} \cdot \text{dm}^{-3} \text{s}^{-1}$$

(y-scale : 0 – 40 $\text{mmol} \cdot \text{dm}^{-3} \text{s}^{-1}$)

$$\text{slope} = \frac{4 \times 10^4}{10 \times 10^2} = 40$$

(x-scale : 0 – 1 $\text{mmol} \cdot \text{dm}^{-3} \text{s}^{-1}$)

$$K_M = \frac{40}{4} = 10 \text{ mmol} \cdot \text{dm}^{-3}$$

$$k_{\text{cat}} = \frac{v_{\max}}{[E]_0} = \frac{2.5 \times 10^{-4}}{2.3 \times 10^{-9}} = 1.1 \times 10^5 \text{ s}^{-1}$$

$$\epsilon = \frac{k_{\text{cat}}}{K_M} = \frac{1.1 \times 10^5}{10^{-2}} = 1.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

turnover frequency or catalytic constant, $k_{cat} = \frac{\text{\#catalytic cycles performed by active site}}{\text{duration of interval}}$
has units of 1st order rate constant

numerically equivalent to k_b in Michaelis-Menten mechanism

$$k_{cat} = k_b = \frac{v_{max}}{[E]_0}$$

$$\text{catalytic efficiency, } \varepsilon = \frac{k_{cat}}{K_M} = \frac{k_a k_b}{k'_a + k_b}$$

Higher $\varepsilon \implies$ more efficient

efficiency is max ($= k_a$) when $k_b \gg k'_a$.

max efficiency related to max rate of diffusion of E and S in solution

\implies rate constants $\approx 10^8 - 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (catalytic perfection)

Inhibitor : decreases rate of product formation from substrate by binding to enzyme, to ES complex, or to enzyme and ES complex simultaneously

$$\text{define: } \alpha = 1 + \frac{[I]}{K_I}$$

$$\alpha' = 1 + \frac{[I]}{K'_I}$$

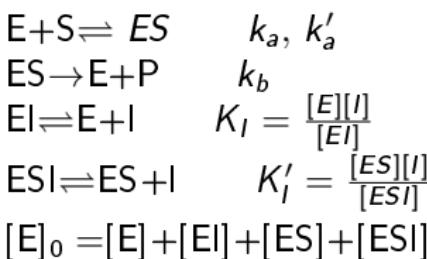
$$[E]_0 = [E]\alpha + [ES]\alpha'$$

$$\text{using } K_M = \frac{[E][S]}{[ES]}$$

$$[E]_0 = \frac{K_M[ES]}{[S]_0} \alpha + [ES]\alpha' = [ES] \left(\frac{\alpha K_M}{[S]_0} + \alpha' \right)$$

$$v = k_b[ES] = \frac{k_b[E]_0}{\frac{\alpha K_M}{[S]_0} + \alpha'} = \frac{v_{max}}{\alpha' + \frac{\alpha K_M}{[S]_0}}$$

$$\text{or, } \frac{1}{v} = \frac{\alpha'}{v_{max}} + \alpha \left(\frac{K_M}{v_{max}} \right) \frac{1}{[S]_0}$$



Lineweaver-Burk plots characteristic of three modes of enzyme inhibition:

competitive inhibition: inhibitor binds only to active site of enzyme and inhibits attachment of substrate; $\alpha > 1$ and $\alpha' = 1$

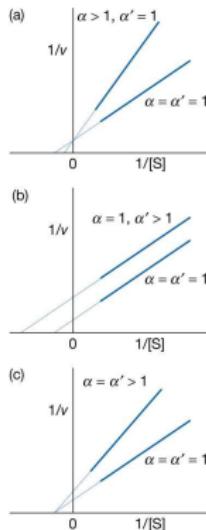
uncompetitive inhibition : inhibitor binds to enzyme site removed from active site, but only if substrate is already present. ESI reduces the concentration of ES (active complex). In this case $\alpha = 1$ (\because EI does not form) and $\alpha' > 1$.

non-competitive (mixed) inhibition : inhibitor binds to site other than active site, and its presence reduces ability of substrate to bind to active site.

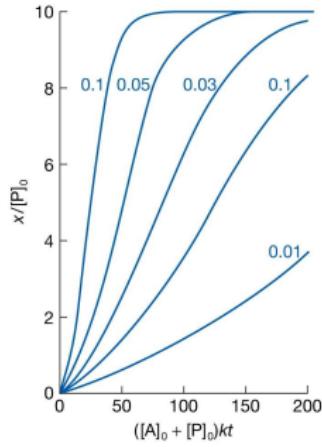
Inhibition occurs at both E and ES sites : $\alpha > 1$ and $\alpha' > 1$.

Slope and y-intercept of Lineweaver-Burk plot increase upon addition of inhibitor. Fig. c : special case : $K_I = K'_I$; and $\alpha = \alpha'$, which results in intersection of lines on x-axis

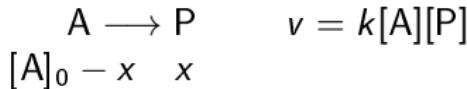
$$\frac{1}{v} = \frac{\alpha'}{v_{max}} + \alpha \left(\frac{K_M}{v_{max}} \right) \frac{1}{[S]_0}$$



Autocatalysis:



labelled by b



$$\frac{dx}{dt} = k ([A]_0 - x) ([P]_0 + x)$$

integrating:

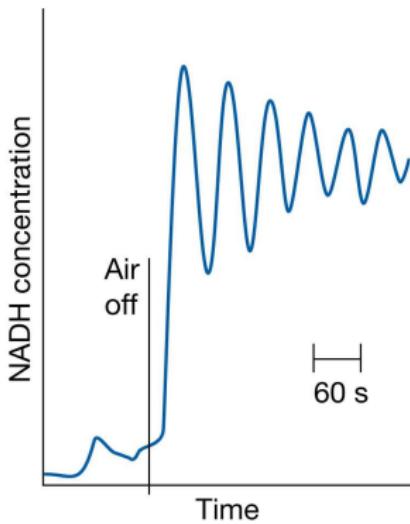
$$\frac{1}{[A]_0 + [P]_0} \ln \frac{([P]_0 + x)[A]_0}{[P]_0([A]_0 - x)} = kt$$

$$\text{or, } \frac{x}{[P]_0} = \frac{e^{at} - 1}{1 + b e^{at}}, \text{ where } a = ([A]_0 + [P]_0) k$$

$$\text{and } b = \frac{[P]_0}{[A]_0}$$

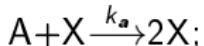
oscillating reactions: Feedback mechanism in which a product either increases or decreases the reaction rate

- can be sustained indefinitely only if the reaction is carried at far from equilibrium conditions (continuous supply and dissipation of species)

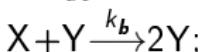


under anaerobic conditions, oscillations in [NADH] can occur in glycolytic cycle in yeast cells because of inhibition of the enzyme phosphofructokinase by high levels of ATP and its activation by high levels of ADP

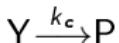
Lotka-Volterra (Prey-predator) mechanism:



$$\frac{d[X]}{dt} = k_a[A][X] - k_b[X][Y]$$



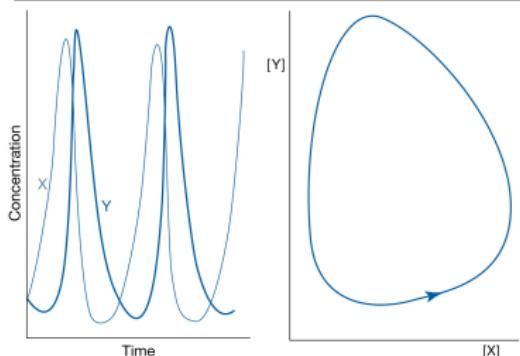
$$\frac{d[Y]}{dt} = k_b[X][Y] - k_c[Y]$$



$$\text{use } [X] = \frac{k_c}{k_b}x; [Y] = \frac{k_c}{k_b}y;$$

$$[A] = \frac{k_c}{k_a}a; t = \frac{1}{k_c}\tau$$

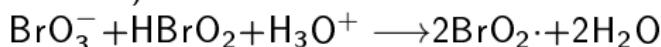
$$\begin{aligned} \frac{dx}{d\tau} &= ax - xy \\ \frac{dy}{d\tau} &= xy - y \end{aligned} \implies \text{s.s. : } (1, a)$$



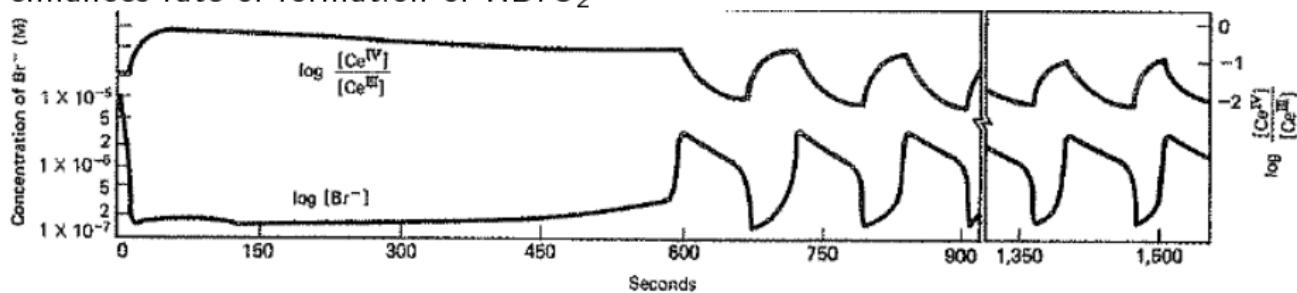
$$\begin{aligned} x &= 1 + \Delta_x e^{\omega\tau} \\ y &= a + \Delta_y e^{\omega\tau} \end{aligned} \implies \begin{pmatrix} \Delta_x \\ \Delta_y \end{pmatrix} = \begin{pmatrix} \omega & 1 \\ a & -\omega \end{pmatrix} \begin{pmatrix} \Delta_x \\ \Delta_y \end{pmatrix}$$

$$\text{or, } \omega = \pm i\sqrt{a}$$

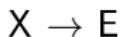
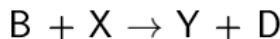
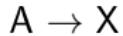
Belousov-Zhabotinski reaction (KBrO₃, malonic acid, cerium (IV) salt in acidic solution):



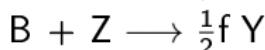
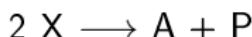
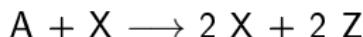
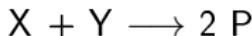
product HBrO₂ is a reactant in first step and provides a feedback mechanism that enhances rate of formation of HBrO₂



<https://en.wikipedia.org/wiki/Brusselator>



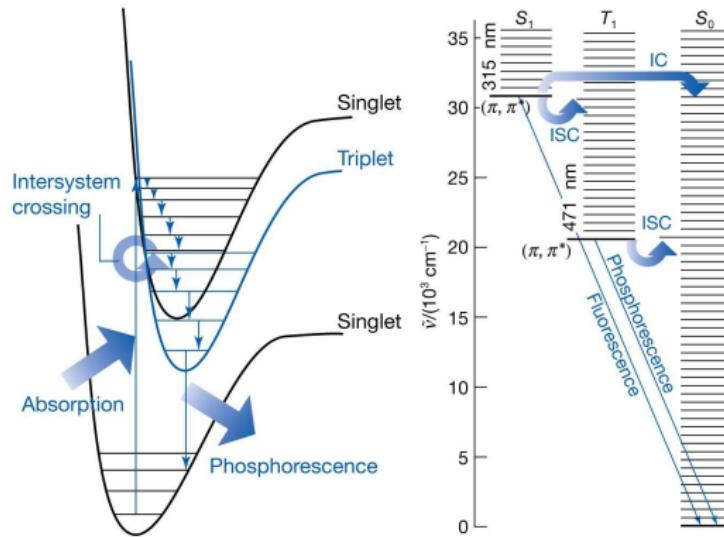
<https://en.wikipedia.org/wiki/Oregonator>



Photochemistry

- ▶ initiated by absorption of electromagnetic radiation
- ▶ most important : processes that capture solar energy
 - ▶ Some reactions lead to the heating of the atmosphere during the daytime by absorption of uv radiation.
 - ▶ Others include absorption of visible radiation during photosynthesis

Jablonski diagram



ground vibrational states correctly located vertically but other vibrational states are shown schematically

(IC: internal conversion; ISC: intersystem crossing)

primary process : products formed directly from excited state of reactant

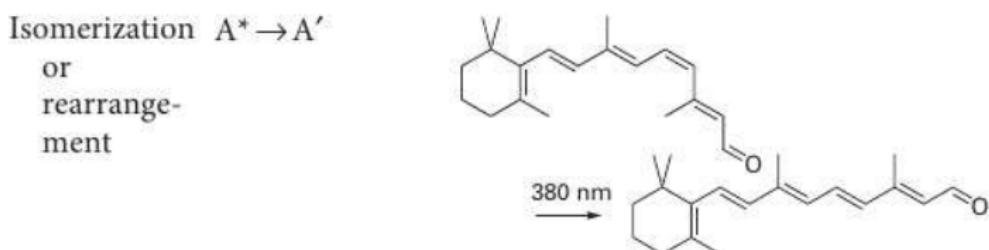
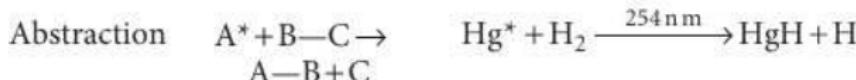
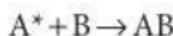
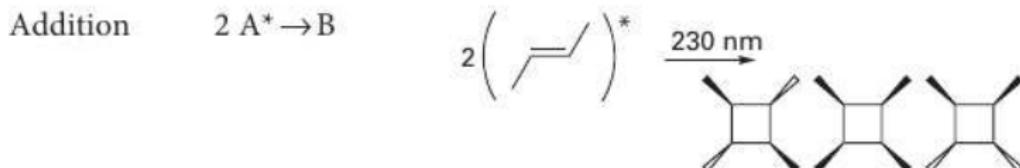
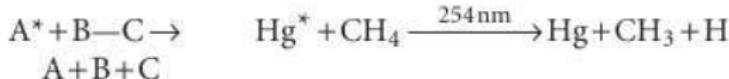
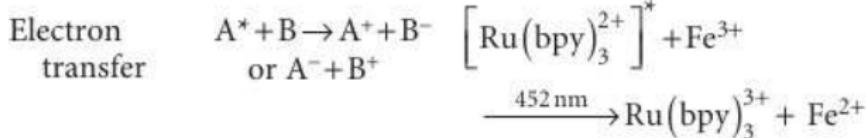
Ex. : fluorescence and cis-trans photoisomerization of retinal

secondary process : products originate from intermediates formed directly from excited state of reactant,

Ex. : oxidative processes initiated by oxygen atom formed by ozone photodissociation

Competing with formation of photochemical products are numerous primary photophysical processes that can deactivate excited state

∴ it is important to consider timescales of formation and decay of excited states before describing mechanisms



Primary absorption	$S + h\nu \rightarrow S^*$
Excited-state absorption	$S^* + h\nu \rightarrow S^{**}$
	$T^* + h\nu \rightarrow T^{**}$
Fluorescence	$S^* \rightarrow S + h\nu$
Stimulated emission	$S^* + h\nu \rightarrow S + 2 h\nu$
Intersystem crossing (ISC)	$S^* \rightarrow T^*$
Phosphorescence	$T^* \rightarrow S + h\nu$
Internal conversion (IC)	$S^* \rightarrow S$
Collision-induced emission	$S^* + M \rightarrow S + M + h\nu$
Collisional deactivation	$S^* + M \rightarrow S + M$
	$T^* + M \rightarrow S + M$
Electronic energy transfer:	
Singlet-singlet	$S^* + S \rightarrow S + S^*$
Triplet-triplet	$T^* + T \rightarrow T + T^*$
Excimer formation	$S^* + S \rightarrow (SS)^*$
Energy pooling	
Singlet-singlet	$S^* + S^* \rightarrow S^{**} + S$
Triplet-triplet	$T^* + T^* \rightarrow S^{**} + S$

Interplay of reaction rates \leftrightarrow excited state lifetime is important in determining kinetic feasibility of photochemical process

Electronic transitions: $10^{-15}\text{s} \implies k_{\text{1st-order}} < 10^{16}\text{s}^{-1}$

$\tau_{\text{fluorescence}} \sim 10^{-12} - 10^{-6}\text{s} > \tau_{\text{absorption}}$

excited singlet state can initiate fast photochemical reactions in $10^{-15} - 10^{-12}\text{ s}$

primary process of vision is complete in 200fs

for large organic molecules: ISC $\sim 10^{-12} - 10^{-4}\text{s}$

and phosphorescence $\sim 10^{-6} - 10^{-1}\text{s}$

\implies excited triplet states are important photochemically; such species can undergo large number of collisions with other reactants before deactivation

Consider

molecular photochemical reaction, $k = 1.7 \times 10^4 \text{ s}^{-1}$

relaxation time $\tau = \frac{1}{1.7 \times 10^4} \text{ s}^{-1} = 59 \mu\text{s}$

reactant with observed fluorescence lifetime = 1 ns

observed phosphorescence lifetime = 1 ms

Excited singlet state is too short-lived and not expected to be major source of product in this reaction.

Excited triplet state is a good candidate for a precursor

Rates of deactivation of excited state : $\left\{ \begin{array}{l} \text{radiative} \\ \text{non-radiative} \\ \text{chemical} \end{array} \right.$
 determine yield of product in a photochemical reaction

Primary quantum yield,

$$\phi = \frac{\#\text{photo-events (physical/chemical)}}{\#\text{photons absorbed in same interval}} = \frac{\text{rate of process(es)}}{\text{intensity of light absorbed (rate of photon absorption)}} = \frac{v}{I_{\text{abs}}}$$

total #molecules deactivated (radiative/non-radiative/photo-reactive)
 = #excited species produced by absorption of light

$$\Rightarrow \sum_i \phi_i = \sum_i \frac{v_i}{I_{\text{abs}}} = 1$$

$$\Rightarrow \phi_f + \phi_{IC} + \phi_{ISC} + \phi_p + \phi_R = 1; \quad \phi_i = \frac{v_i}{\sum_i v_i}$$

ex. : absorbing substance exposed to 490 nm light

from a $P = 100$ W source

for 2700 s

with $f = 60\%$ of incident light absorbed

0.344 mol of absorbing substance decomposed

$\phi = ?$

$$E_{abs} = fPt = N_{abs} \frac{hc}{\lambda}, \text{ or, } N_{abs} = \frac{fPt\lambda}{hc}$$

$$\phi = \frac{N_{\text{decomposed}}}{N_{\text{absorbed}}} = \frac{(0.344 \times 6.023 \times 10^{23}) \times 6.626 \times 10^{-34} \times 2.998 \times 10^8}{0.6 \times 100 \times 2700 \times 490 \times 10^{-9}} = 0.52$$

Mechanism of decay of excited singlet states

Absorption: $S + h\nu_i \rightarrow S^*$; $v_{abs} = I_{abs}$

Fluorescence: $S^* \rightarrow S + h\nu_f$; $v_f = k_f[S^*]$

Internal conversion: $S^* \rightarrow S$; $v_{IC} = k_{IC}[S^*]$

Intersystem crossing: $S^* \rightarrow T^*$; $v_{ISC} = k_{ISC}[S^*]$

rate of formation of $S^* = I_{abs}$

rate of decay of $S^* = -k_f[S^*] - k_{ISC}[S^*] - k_{IC}[S^*]$

$$= -(k_f + k_{ISC} + k_{IC})[S^*]$$

Assuming first order process:

$$[S^*]_t = [S^*]_0 e^{-\frac{t}{\tau_0}}; \quad \tau_0 = \frac{1}{k_f + k_{ISC} + k_{IC}}$$

rate of formation of $S^* = I_{\text{abs}}$

rate of decay of $S^* = -k_f[S^*] - k_{\text{ISC}}[S^*] - k_{\text{IC}}[S^*]$

$$\frac{d[S^*]}{dt} = I_{\text{abs}} - (k_f + k_{\text{ISC}} + k_{\text{IC}})[S^*] = 0 \quad (\text{S.S.})$$

or, $I_{\text{abs}} = (k_f + k_{\text{ISC}} + k_{\text{IC}})[S^*]$

Quantum yield of fluorescence, $\phi_f = \frac{v_f}{I_{\text{abs}}} = \frac{k_f[S^*]}{(k_f + k_{\text{ISC}} + k_{\text{IC}})[S^*]} = \frac{k_f}{k_f + k_{\text{ISC}} + k_{\text{IC}}}$

Fluorescence lifetime can be measured with pulsed laser technique.

Sample is excited with a short light pulse from a laser using wavelength at which S absorbs strongly

exponential decay of fluorescence intensity after pulse is monitored

$$\tau_0 = \frac{1}{k_f + k_{\text{ISC}} + k_{\text{IC}}} = \frac{k_f}{k_f + k_{\text{ISC}} + k_{\text{IC}}} \times \frac{1}{k_f} = \frac{\phi_f}{k_f}$$

tryptophan in water: $\phi_f = 0.20$; $\tau_0 = 2.6 \text{ ns}$

$$\therefore k_f = \frac{\phi_f}{\tau_0} = \frac{0.20}{2.6 \times 10^{-9} \text{ s}} = 7.7 \times 10^7 \text{ s}^{-1}$$

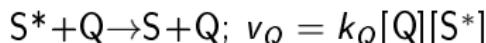
Quenching: shortening of lifetime of excited state

- either a desired process, e.g., in energy or electron transfer

or an undesired side reaction decreasing quantum yield of desired photochemical process

Quenching effects are studied by monitoring emission from excited state involved in photochemical reaction

Addition of quencher, Q, opens additional channel for deactivation:



$$\frac{d[S^*]}{dt} = I_{\text{abs}} - (k_f + k_{\text{ISC}} + k_{\text{IC}} + k_Q [Q]) [S^*] = 0$$

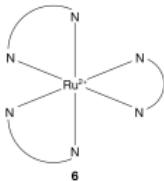
$$\phi_f = \frac{k_f}{k_f + k_{\text{ISC}} + k_{\text{IC}} + k_Q [Q]} = \tau k_f$$

$$\text{for } [Q] = 0, \phi_{f,0} = \frac{k_f}{k_f + k_{\text{ISC}} + k_{\text{IC}}} = \tau_0 k_f$$

$$\frac{\phi_{f,0}}{\phi_f} = \frac{\tau_0}{\tau} = \frac{k_f + k_{\text{ISC}} + k_{\text{IC}} + k_Q [Q]}{k_f + k_{\text{ISC}} + k_{\text{IC}}} = 1 + \frac{k_Q}{k_f + k_{\text{ISC}} + k_{\text{IC}}} [Q]$$

$$= 1 + \tau_0 k_Q [Q] : \text{Stern-Volmer equation}$$

The molecule 2,2'-bipyridine forms a complex with the Ru^{2+}

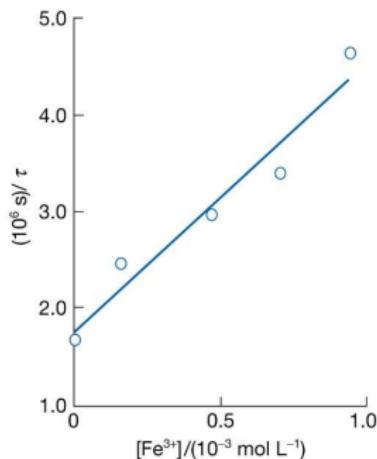


$\text{Ru}(\text{bipy})_3^{2+}$ has strong metal-to-ligand charge transfer (MLCT) transition at 450 nm.

Quenching of the ${}^*\text{Ru}(\text{bipy})_3^{2+}$ excited state by $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in acidic solution monitored by measuring emission lifetimes at 600 nm.

$[\text{Fe}(\text{H}_2\text{O})_6^{3+}] / (10^{-4} \text{ mol dm}^{-3})$	0	1.6	4.7	7	9.4
$\tau / (10^{-7} \text{ s})$	6	4.05	3.37	2.96	2.17

data:



$$\frac{\tau_0}{\tau} = 1 + \tau_0 k_Q [Q];$$

$$\text{slope} = 2.8 \times 10^9 = k_Q (\text{in } \text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$$

Common mechanisms for bimolecular quenching :

Collisional deactivation: $S^* + Q \rightarrow S + Q$

Resonance energy transfer: $S^* + Q \rightarrow S + Q^*$

Electron transfer: $S^* + Q \rightarrow S^+ + Q^-$ or $S^- + Q^+$

Collisional quenching : particularly efficient when Q is a heavy species, such as I^- , which receives energy from S^* and decays primarily by internal conversion to ground state

This fact is used to determine the accessibility of amino acid residues of a folded protein to solvent

- fluorescence from tryptophan residue ($\lambda_{abs} = 290$ nm, $\lambda_{fluor} = 350$ nm) is quenched by I^- ion when residue is on surface of protein and hence accessible to solvent.

Conversely, residues in hydrophobic interior of protein are not quenched effectively by I^-

Quenching rate constant itself does not give much insight into mechanism of quenching

Quenching of excited state of $Ru(bipy)_3^{2+}$ is a result of light-induced electron transfer to Fe^{3+} , but quenching data do not prove the mechanism

resonance energy transfer (RET): $S^* + Q \rightarrow S + Q^*$

Oscillating electric field of incoming radiation induces oscillating electric dipole moment in S

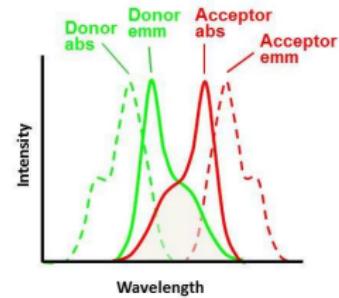
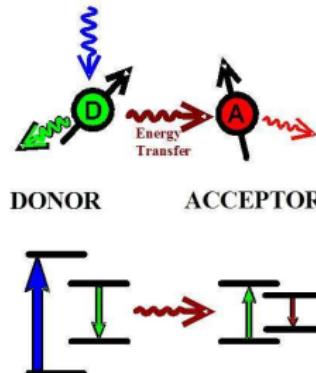
Energy is absorbed by S if frequency of incident radiation $\nu = \frac{\Delta E_s}{h}$, where ΔE_s = energy separation between ground and excited electronic states of S : 'resonance'

Oscillating dipole on S affects electrons bound to nearby Q molecule by inducing oscillating dipole moment in Q.

If frequency of oscillation of dipole moment in S is $\nu = \frac{\Delta E_Q}{h}$, then Q absorbs energy from S

RET Efficiency : $E_T = 1 - \frac{\phi_f}{\phi_{f,0}}$

Fluorescence Resonance Energy Transfer (FRET)

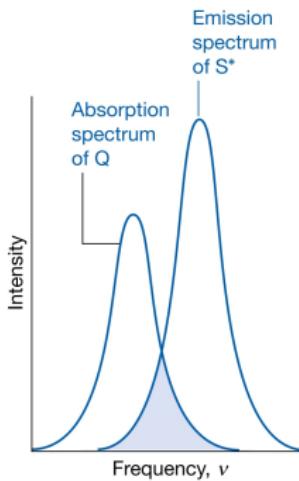


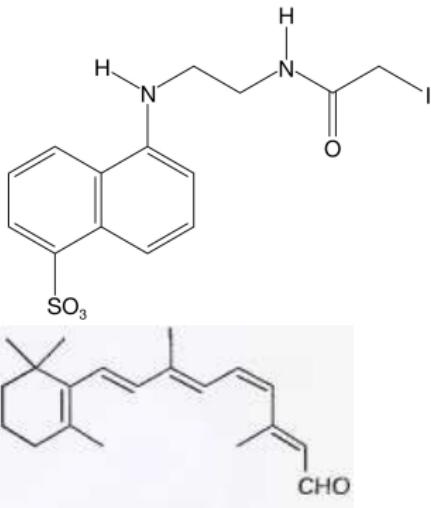
Förster theory (1959)

energy transfer is efficient when:

- ▶ Energy donor and acceptor are separated by short distance, \mathcal{O} (1 nm)
- ▶ Photons emitted by excited state of donor can be absorbed directly by acceptor.
- ▶ $E_T = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6}$, R in nm and R_0 is a parameter

Donor ^T	Acceptor	R_0 /nm
Naphthalene	Dansyl	2.2
Dansyl	ODR	4.3
Pyrene	Coumarin	3.9
IEDANS	FITC	4.9
Tryptophan	IEDANS	2.2
Tryptophan	Haem (heme)	2.9





FRET:

When an amino acid on surface of rhodopsin was labelled covalently with energy donor 1,5-I AEDANS,

fluorescence quantum yield of label decreased from 0.75 to 0.68 due to quenching by visual pigment 11-cis-retinal.

$$E_T = 1 - \frac{0.68}{0.75} = 0.093$$

using known value of $R_0 = 5.4 \text{ nm}$ for 1,5-I AEDANS/11-cis-retinal pair,
we get $R = 7.9 \text{ nm}$

criteria governing relative efficiencies of collisional quenching, resonance energy transfer, and electron transfer:

Collisional quenching : particularly efficient when Q, e.g., I^- , receives energy from S^* and decays to ground state primarily by releasing heat

Electron transfer reactions : Marcus theory (1965) :

rates of electron transfer (from ground or excited states) depend on:

- ▶ distance between donor (D) and acceptor (A) ; becoming more efficient as D-A distance decreases
- ▶ $\Delta_r G$; e-transfer is more efficient as reaction becomes more exergonic, e.g., for efficient photo oxidation of S, reduction potential of S^* must be lower than that of Q
- ▶ **reorganization energy** (energy cost incurred by molecular rearrangements of D, A, and medium) :
electron transfer rate predicted to increase as reorganization energy is matched closely by reaction Gibbs energy

Electron transfer can be studied by time-resolved spectroscopy.

Oxidized and reduced products often have electronic absorption spectra distinct from those of neutral parent compounds. Rapid appearance of such known features in absorption spectrum after excitation by laser pulse may be taken as indication of quenching by electron transfer

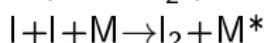
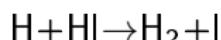
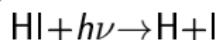
Overall quantum yield of a photochemical reaction

For complex reactions involving secondary processes,

e.g., chain reactions initiated by photolysis, many reactant molecules may be consumed as a result of absorption of single photon.

Overall quantum yield, Φ , # reactant molecules consumed per photon absorbed, may exceed 1.

photolysis of HI:



\therefore absorption of 1 photon leads to destruction of 2 HI molecules

\therefore Overall quantum yield = 2

In chain reactions, Φ may be very large : values $\sim 10^4$ are common
the chain acts as chemical amplifier of initial absorption step

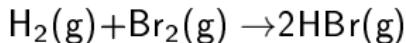
4-heptanone irradiated
for 100 s
with 313 nm radiation
with a power output of 50 W
under conditions of total absorption,
2.8 mmol C_2H_4 formed.

amount (in moles) of photons absorbed, $n = \frac{P\Delta t}{(\frac{hc}{\lambda})N_A}$

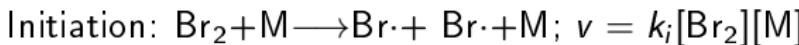
$$\Phi = \frac{nc_{2H_4}}{n} = \frac{nc_{2H_4} N_A hc}{\lambda P \Delta t} = \frac{2.8 \times 10^{-3} \times 6.023 \times 10^{23} \times 6.636 \times 10^{-34} \times 2.998 \times 10^8}{3.13 \times 10^{-7} \times 50 \times 100} = 0.21$$

Rate laws of complex photochemical reactions:

consider photochemical activation of chain reaction



Earlier for thermal reaction,



now: $\text{Br}_2 + h\nu \rightarrow \text{Br}\cdot + \text{Br}\cdot$ $v = I_{abs} = \frac{\text{# photons absorbed}}{\text{volume in which absorption occurs} \times \text{time interval}}$

Earlier, we had:

$$\frac{d[\text{HBr}]}{dt} = 2k_{p'}[\text{H}][\text{Br}_2] = \frac{2k_p \sqrt{\frac{k_t}{k_r}} [\text{H}_2][\text{Br}_2]^{\frac{3}{2}}}{[\text{Br}_2] + \frac{k_r}{k_{p'}} [\text{HBr}]} = \frac{k[\text{H}_2][\text{Br}_2]^{\frac{3}{2}}}{[\text{Br}_2] + k'[\text{HBr}]}$$

now: I_{abs} should take the place of $k_i[\text{Br}_2][\text{M}]$

$$\frac{d[\text{HBr}]}{dt} = 2k_{p'}[\text{H}][\text{Br}_2] = \frac{2k_p \sqrt{\frac{1}{k_t[\text{M}]}} [\text{H}_2][\text{Br}_2] \sqrt{I_{abs}}}{[\text{Br}_2] + \frac{k_r}{k_{p'}} [\text{HBr}]} = \frac{k[\text{H}_2][\text{Br}_2]}{[\text{Br}_2] + k'[\text{HBr}]} \sqrt{I_{abs}}$$

photosensitization:

Reactions of a molecule that does not absorb directly can be made to occur if another absorbing molecule is present

because latter may be able to transfer its energy to former during a collision

e.g., generation of excited state O_2 in photodynamic therapy:

laser radiation delivered to diseased tissue through a fibre optic cable absorbed by a drug which, in its first excited triplet state 3P , photosensitizes the formation of excited 1O_2

Absorption: $P + h\nu \rightarrow P^*$

ISC: $P^* \rightarrow ^3P$

Photosensitization: $^3P + ^3O_2 \rightarrow P + ^1O_2$

1O_2 molecules are very reactive and destroy cellular components and it is thought that cell membranes are primary cellular targets

Photosensitization: $^3P + ^3O_2 \rightarrow P + ^1O_2$

Oxidation reactions: $^1O_2 + \text{reactants} \rightarrow \text{products}$

example: $P \equiv \text{Haematoporphyrin}$; characteristics ?

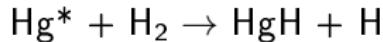
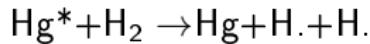
Another example :

generation of atomic H,

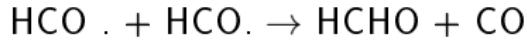
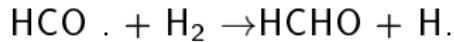
irradiation of H_2 gas containing trace of Hg vapour using radiation of 254 nm from a Hg discharge lamp

The Hg atoms are excited (to Hg^*) by resonant absorption of radiation

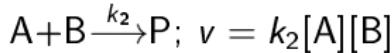
and then collide with H_2 molecules.



The latter reaction is the initiation step for other mercury photosensitized reactions, such as synthesis of formaldehyde from carbon monoxide and hydrogen:
 $H + CO \rightarrow HCO$.



last step is termination by disproportionation rather than by combination

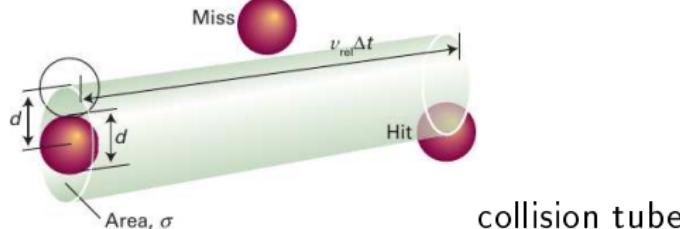
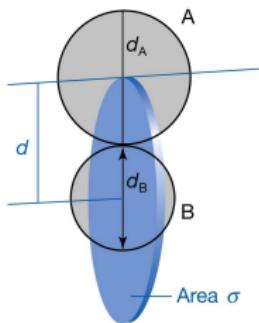


speed ↓
crossecn. ↓
mols ↓
v \propto steric requirement (P) \times encounter rate $\left(\sigma \cdot \sqrt{\frac{T}{M}} \cdot [A][B] \right) \times \left(e^{-\frac{E_a}{RT}} \right)$
fraction with min. energy

count 'hit' whenever centres of two molecules come within distance d of each other

$$d \text{ (collision diameter)} = \frac{1}{2} (d_A + d_B)$$

collision frequency, $z = \frac{\text{\#collisions made by a molecule}}{\text{time interval of collisions}}$



mean relative speed \bar{v}_{rel} for time Δt , cross-sectional area $\sigma = \pi d^2$,

$$\text{length traveled} = \bar{v}_{\text{rel}} \Delta t, \text{ volume} = \sigma \bar{v}_{\text{rel}} \Delta t$$

#stationary molecules with centres inside collision tube

$$= \frac{N}{V} \sigma \bar{v}_{\text{rel}} \Delta t \implies z = \frac{N}{V} \sigma \bar{v}_{\text{rel}}; \bar{v}_{\text{rel}} = \sqrt{\frac{8k_B T}{\pi \mu}}; \mu = \frac{m}{2}$$

Total collision density, $Z_{AA} = \frac{1}{2} z \frac{N_{(A)}}{V} = \frac{1}{2} \sigma \bar{v}_{\text{rel}} \left(\frac{N_{(A)}}{V} \right)^2$

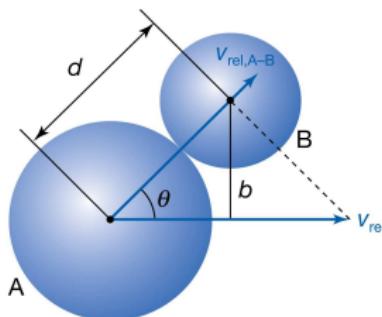
and $Z_{AB} = z \frac{N_{(B)}}{V} = \sigma \bar{v}_{\text{rel}} \left(\frac{N_{(A)} N_{(B)}}{V^2} \right)$

energy requirement: $\sigma(\varepsilon) = 0 \forall \varepsilon < \varepsilon_a$

$$\therefore \frac{d[A]}{dt} = -\sigma(\varepsilon) v_{\text{rel}} N_A[A][B]; v_{\text{rel}} = \sqrt{\frac{2\varepsilon}{\mu}}$$

for a wide range of approach energies,

$$\frac{d[A]}{dt} = - \left\{ \int_0^{\infty} \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon \right\} N_A[A][B] \implies k_2 = N_A \int_0^{\infty} \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon$$

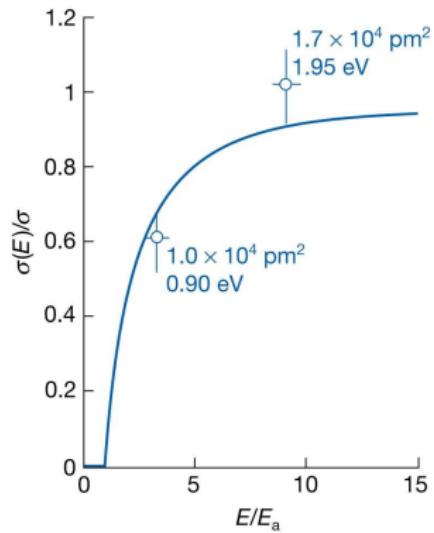


$$v_{\text{rel}, A-B} = v \cos \theta = v_{\text{rel}} \sqrt{\frac{d^2 - b^2}{d^2}} \implies \varepsilon_{A-B} = \varepsilon \frac{d^2 - b^2}{d^2}$$

$\forall b > b_{\text{max}}$, reaction does not occur

$$\varepsilon_a = \varepsilon \frac{d^2 - b_{\text{max}}^2}{d^2} \implies b_{\text{max}}^2 = \left(1 - \frac{\varepsilon_a}{\varepsilon}\right) d^2$$

$$\implies \forall \varepsilon > \varepsilon_a, \sigma(\varepsilon) = \left(1 - \frac{\varepsilon_a}{\varepsilon}\right) \sigma$$



Maxwell-Boltzmann distribution:

$$f(v)dv = 4\pi \left(\frac{\mu}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} dv = 2\pi \left(\frac{1}{\pi k_B T} \right)^{\frac{3}{2}} \sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon = f(\varepsilon) d\varepsilon$$

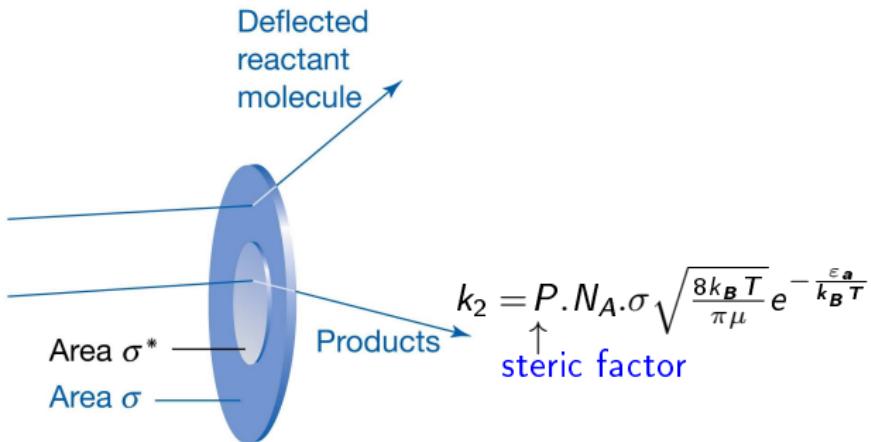
$$\therefore \int_0^{\infty} \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon = 2\pi \left(\frac{1}{\pi k_B T} \right)^{\frac{3}{2}} \int_0^{\infty} \sigma(\varepsilon) \sqrt{\frac{2\varepsilon}{\mu}} \sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$= \sqrt{\frac{8}{\pi \mu k_B T}} \left(\frac{1}{k_B T} \right) \underbrace{\int_0^{\infty} \varepsilon \sigma(\varepsilon) e^{-\frac{\varepsilon}{k_B T}} d\varepsilon}_{\text{underbrace}}$$

$$\sigma \int_{\varepsilon_a}^{\infty} \varepsilon \left(1 - \frac{\varepsilon_a}{\varepsilon}\right) e^{-\frac{\varepsilon}{k_B T}} d\varepsilon = (k_B T)^2 \sigma e^{-\frac{\varepsilon_a}{k_B T}}$$

$$\therefore k_2 = N_A \int_0^{\infty} \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon = N_A \sigma \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{\varepsilon_a}{k_B T}}$$

	$A/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$			
	Experiment	Theory	$E_a/(\text{kJ mol}^{-1})$	P
$2 \text{NOCl} \rightarrow 2 \text{NO} + 2 \text{Cl}$	9.4×10^9	5.9×10^{10}	102	0.16
$2 \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	6.3×10^7	2.5×10^{10}	0	2.5×10^{-3}
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	1.24×10^6	7.4×10^{11}	180	1.7×10^{-6}
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	1.0×10^{12}	2.1×10^{11}	0	4.8





$$\mu = \frac{m_1 m_2}{m_1 + m_2} = 3.12 \times 10^{-27} \text{ kg}$$

$$\sqrt{\frac{8k_B T}{\pi \mu}} = 2.66 \times 10^3 \text{ ms}^{-1}; \sigma_{\text{H}_2} = 0.27 \text{ nm}^2; \sigma_{\text{C}_2\text{H}_4} = 0.64 \text{ nm}^2$$

$$\text{mean } \sigma = 0.46 \text{ nm}^2$$

$$A = \sigma \sqrt{\frac{8k_B T}{\pi \mu}} N_A = 7.37 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\text{exp. } A = 1.24 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \implies P = 1.7 \times 10^{-6}$$

Generally, more complex the molecules, the smaller the value of P



harpoon mechanism:

Distance of approach at
which reaction occurs \gg

distance needed for deflection of path of
approaching molecules in non-reactive collision

Harpoon: K atom approaches Br_2 molecule,
when they are close enough an electron
(harpoon) flips across from K to Br_2

In place of two neutral particles there are two ions
with Coulombic attraction between them
: line on the harpoon

Under its influence ions move together
(line wound in), reaction takes place
 $\implies KBr + Br$



harpoon extends the cross-section for reactive encounter

Estimating steric factor, P , for harpoon mechanism:
net change in energy when transfer of charge occurs at separation R :

$$E = I - E_{ea} - \frac{e^2}{4\pi\epsilon_0 R}$$

$$I > E_{ea} \implies E < 0 \text{ iff } R < R^* \text{ s.t. } \frac{e^2}{4\pi\epsilon_0 R^*} = I - E_{ea}$$

At $R = R^*$, harpoon shoots across from K to Br₂,

$$\therefore \sigma^* = \pi R^{*2}$$

$$\implies P = \frac{\sigma^*}{\sigma} = \left[\frac{e^2}{4\pi\epsilon_0 d(I - E_{ea})} \right]^2 \text{ where } d = R(K) + R(\text{Br}_2)$$

$$I = 420 \text{ kJ.mol}^{-1}, E_{ea} = 250 \text{ kJ.mol}^{-1} \text{ and } d = 400 \text{ pm}$$

$$\implies P = 4.2 \text{ (Exp. P= 4.8)}$$

Diffusion-controlled reactions:

Encounters between reactants in solution occur in very different manner from encounters in gases

Reactant molecules have to jostle through the solvent
encounter frequency is considerably less than in gas

However, because a molecule migrates only slowly away from a location,
reactant molecules that encounter each other stay near each other for much
longer than in a gas

cage effect: Lingering of one molecule near another

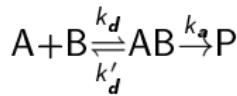
on account of hindering presence of solvent molecules

encounter pair may accumulate enough energy to react even though it does not
have enough energy to do so when it first forms

Activation energy is more complicated in solution than in gas

because encounter pair is surrounded by solvent

we must consider energy of entire local assembly of reactant and solvent molecules



$$\text{ss: } \frac{d[AB]}{dt} = k_d[A][B] - k'_d[AB] - k_a[AB] \approx 0$$

$$\implies [AB] = \frac{k_d[A][B]}{k_a + k'_d}$$

$$\text{rate: } \frac{d[P]}{dt} = k_a[AB] = k_2[A][B]; \quad k_2 = \frac{k_a k_d}{k_a + k'_d}$$

$k'_d \ll k_a \implies k_2 = k_d$: diffusion-controlled limit [$k \sim \mathcal{O}(10^9) \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$]

$k'_d \gg k_a \implies k_2 = \frac{k_a k_d}{k'_d} = k_a K$: activation-controlled limit

- reaction proceeds at the rate at which energy accumulates in the encounter pair from surrounding solvent

	Solvent	$A/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_a/(\text{kJ mol}^{-1})$
$(\text{CH}_3)_3\text{CCl}$ solvolysis	Water	7.1×10^{16}	100
	Ethanol	3.0×10^{15}	112
	Chloroform	1.4×10^4	45
$\text{CH}_3\text{CH}_2\text{Br}$	Ethanol	4.3×10^{11}	90

in 3-D, diffusion eq. : $\frac{dc}{dt} = \nabla^2 c$

ss: $\nabla^2 c = 0$ and spherical symmetry $\implies \frac{d^2 c}{dr^2} + \frac{2}{r} \frac{dc}{dr} = 0$

General soln. : $c(r) = a + \frac{b}{r}$

B.c. : $\forall r \rightarrow \infty, c \rightarrow c_{\text{bulk}}$ (call it c); then $a = c$

Also, at some $r = R^*$, reaction occurs and $c = 0$

then $c + \frac{b}{R^*} = 0 \implies b = -R^*c$

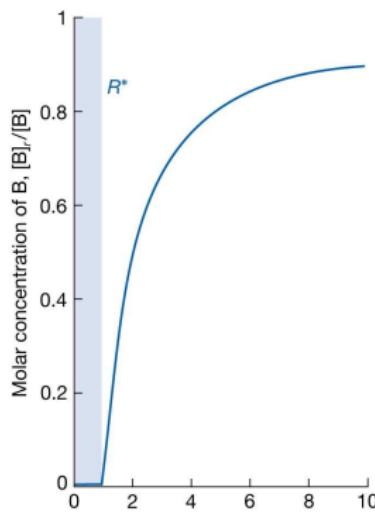
$\therefore c(r) = \left(1 - \frac{R^*}{r}\right)c$

reaction rate = spherical surface of radius $R^* \times J$ (flux of B approaching A)

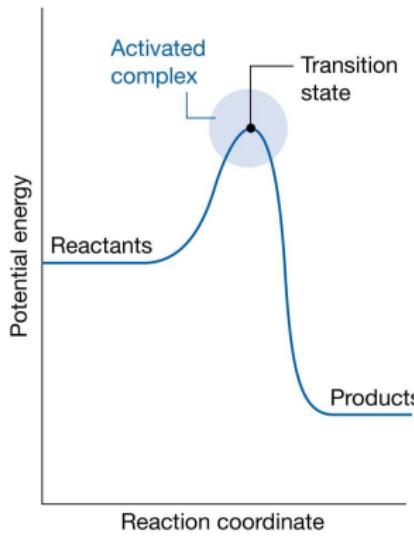
$$= 4\pi R^{*2} J$$

and by Fick's first law: $J = D \left(\frac{dc}{dr} \right)_{r=R^*} = \frac{Dc}{R^*}$

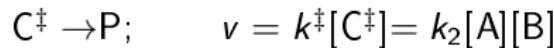
Hence : rate of reaction = $4\pi R^* Dc$



$$[B]_r = \left(1 - \frac{R^*}{r}\right)[B]$$



$$[C^\ddagger] = \frac{RT}{p^\ominus} K^\ddagger [A][B]$$



$$\text{or, } k_2 = \frac{RT}{p^\ominus} k^\ddagger K^\ddagger$$

Activated complex forms products if it passes through TS

If its vibration-like motion along reaction coordinate occurs with frequency ν

then frequency with which the complex approaches TS is also ν

It is possible that **not every** oscillation along reaction coordinate takes the complex through TS

centrifugal effect of rotations might also be an important contribution to break-up of complex

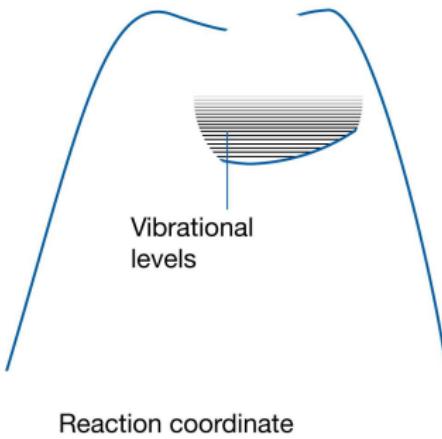
and in some cases complex might be rotating too slowly, or rotating rapidly but about a wrong axis

\therefore rate of passage of complex through TS \propto vibrational frequency along reaction coordinate,

$$k^\ddagger = \kappa \nu ; \kappa = \text{transmission coefficient}$$

there is a broad, shallow dip in PES along reaction coordinate
- complex vibrates harmonically and almost classically in this well
In many cases there is no dip at the top of the barrier
curvature of potential energy, $\frac{d^2V}{dR^2} < 0 \implies$ force constant < 0

\implies imaginary vibrational frequency



Equilibrium constant - statistical expression:

For a reaction $aA + bB + \dots \rightarrow cC + dD + \dots$

$$\Delta_r G^\ominus = [cG_m^\ominus(C) + dG_m^\ominus(D) + \dots] - [aG_m^\ominus(A) + bG_m^\ominus(B) + \dots]$$

$$G = G(0) - nRT \ln \frac{q_m}{N_A}; \quad G(0) = U(0); \quad q_m = \frac{q}{n(\text{mol})}; \quad q = \sum_i e^{-\beta \epsilon_i}; \quad \beta = \frac{1}{k_B T}$$

$$\Delta_r G^\ominus = \Delta_r G(0) - RT \ln \frac{\left(\frac{q_C^\ominus, m}{N_A}\right)^c \left(\frac{q_D^\ominus, m}{N_A}\right)^d \dots}{\left(\frac{q_A^\ominus, m}{N_A}\right)^a \left(\frac{q_B^\ominus, m}{N_A}\right)^b \dots} = -RT \ln K$$

$$K = \frac{\left(\frac{q_C^\ominus, m}{N_A}\right)^c \left(\frac{q_D^\ominus, m}{N_A}\right)^d \dots}{\left(\frac{q_A^\ominus, m}{N_A}\right)^a \left(\frac{q_B^\ominus, m}{N_A}\right)^b \dots} \cdot e^{-\frac{\Delta E_0}{RT}}$$

For formation of the activated complex, $A + B \rightleftharpoons C^\ddagger$

$$K^\ddagger = \frac{N_A q_{C^\ddagger}^\ominus}{q_A^\ominus q_B^\ominus} e^{-\frac{\Delta E_0}{RT}}; \quad \Delta E_0 = E_0(C^\ddagger) - E_0(A) - E_0(B); \quad q = q_{\text{tr}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{el}}$$

$$K = \frac{\left(\frac{q_C^\ominus, m}{N_A}\right)^c \left(\frac{q_D^\ominus, m}{N_A}\right)^d \dots}{\left(\frac{q_A^\ominus, m}{N_A}\right)^a \left(\frac{q_B^\ominus, m}{N_A}\right)^b \dots} \cdot e^{-\frac{\Delta E_0}{RT}}$$

For a given vibration, $\epsilon_i = (i + \frac{1}{2}) h\nu$; $i = 0, 1, 2, \dots$

then for this particular mode, say, v^\ddagger $q_{v^\ddagger} = \sum_i e^{-\beta \epsilon_i} = \sum_{i=0}^{\infty} e^{-\beta(i + \frac{1}{2})h\nu}$

or, $q_{v^\ddagger} = e^{-\frac{1}{2}\beta h\nu} (1 + x + x^2 + \dots)$; $x = e^{-\beta h\nu}$

or, $q_{v^\ddagger} = \frac{e^{-\frac{1}{2}\beta h\nu}}{1 - e^{-\beta h\nu}}$

We absorb the numerator, $e^{-\frac{1}{2}\beta h\nu}$ in the factor $e^{-\frac{\Delta E_0}{RT}}$

The special vibration that leads to formation of product is taken out of all factors in expression for K

also, assuming $\frac{h\nu}{k_B T} \ll 1$, we have $q_{v^\ddagger} = \frac{e^{-\frac{1}{2}\beta h\nu}}{1-e^{-\beta h\nu}} \approx \frac{1}{1-(1-\beta h\nu+\dots)} = \frac{k_B T}{h\nu}$

or, $q_{C^\ddagger} = \frac{k_B T}{h\nu} \tilde{q}_{C^\ddagger}$, where \tilde{q} is partition function without the factor coming from special vibration v^\ddagger of activated complex leading to products

$$\text{write, } K^\ddagger = \frac{k_B T}{h\nu} \tilde{K}^\ddagger; \quad \tilde{K}^\ddagger = \frac{N_A \tilde{q}_{C^\ddagger}^\ominus}{q_A^\ominus q_B^\ominus} e^{-\frac{\Delta E_0}{RT}}$$

$$\text{rate constant, } k_2 = k^\ddagger K^\ddagger = k^\ddagger \frac{k_B T}{h\nu} \tilde{K}_c^\ddagger; \quad \tilde{K}_c^\ddagger = \frac{RT}{p^\ominus} \tilde{K}^\ddagger$$

using $k^\ddagger = \kappa \nu$, we get, Eyring equation:

$$k_2 = \kappa \frac{k_B T}{h} \tilde{K}_c^\ddagger$$

Difficulty with Eyring equation: calculation of partition function of activated complex, C^\ddagger , is difficult to investigate spectroscopically

In general we need to make assumptions about its size, shape, and structure

Collision of **structureless** particles: $A + B \rightleftharpoons C^\ddagger \rightarrow P$

$$q_{J, \text{translation}}^\ominus = \sum_i e^{-\beta \epsilon_i} = \sum_{n_x, n_y, n_z} e^{-\beta \frac{n^2 h^2}{8mL^2}} = \left(\int_0^\infty dn e^{-\beta \frac{n^2 h^2}{8mV^{\frac{2}{3}}}} \right)^3 = \frac{V_m^\ominus}{\Lambda_J^3};$$

$$\text{where } \Lambda_J = \frac{h}{\sqrt{2\pi m_J k_B T}} \text{ and } V_m^\ominus = \frac{RT}{p^\ominus}$$

For activated complex, $m_C = m_A + m_B$ and there are 3 translations.

Lone A–B vibrational mode does not appear in \tilde{q}_{C^\ddagger}

$$\tilde{q}_{C^\ddagger, \text{rot}} = \sum_j e^{-\beta \epsilon_j} = \sum_j e^{-\beta hcBj(j+1)}; \quad hcB = \frac{\hbar^2}{2I}$$

$$= \int_0^\infty dj \cdot (2j+1) e^{-\beta hcBj(j+1)} = \int_0^\infty dx e^{-\beta hcBx} = \frac{2Ik_B T}{\hbar^2}$$

$$\therefore \tilde{q}_{C^\ddagger} = q_{C^\ddagger, \text{translation}}^\ominus \cdot \tilde{q}_{C^\ddagger, \text{rot}} = \left(\frac{2Ik_B T}{\hbar^2} \right) \frac{V_m^\ominus}{\Lambda_{C^\ddagger}^3}$$

For A and B each, we have 3 translations only

$$\begin{aligned} \therefore k_2 &= \kappa \frac{k_B T R T}{h p^\ominus} \left(\frac{2Ik_B T}{\hbar^2} \right) \left(\frac{N_A \Lambda_A^3 \Lambda_B^3}{\Lambda_{C^\ddagger}^3 V_m^\ominus} \right) e^{-\frac{\Delta E_0}{RT}} \\ &= \kappa \frac{k_B T}{h} N_A \left(\frac{2Ik_B T}{\hbar^2} \right) \left(\frac{\Lambda_A \Lambda_B}{\Lambda_{C^\ddagger}} \right)^3 e^{-\frac{\Delta E_0}{RT}} = \kappa N_A \sqrt{\frac{8k_B T}{\pi \mu}} \pi r^2 e^{-\frac{\Delta E_0}{RT}} \\ &= \sigma^* N_A \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{\Delta E_0}{RT}}; \text{ where } \sigma^* = \kappa \pi r^2 \end{aligned}$$

Statistical thermo version of TST runs into difficulties
only in some cases anything is known about structure of activated complex.
However, concept of equilibrium between reactants and activated complex,
motivated a general, empirical approach in which activation process is
expressed in terms of thermodynamic function

$$\Delta^\ddagger G = -RT \ln \tilde{K}^\ddagger$$

$$\text{rate constant: } k_2 = \kappa \frac{k_B T}{h} \frac{RT}{p^\ominus} e^{-\frac{\Delta^\ddagger G}{RT}} = B e^{\frac{\Delta^\ddagger S}{R}} \cdot e^{-\frac{\Delta^\ddagger H}{RT}}; \quad B = \kappa \frac{k_B T}{h} \frac{RT}{p^\ominus}$$

$$\text{activation energy, } E_a = RT^2 \left(\frac{\partial \ln k_2}{\partial T} \right) = \Delta^\ddagger H + 2RT$$

$$\text{or, } k_2 = e^2 B e^{\frac{\Delta^\ddagger S}{R}} e^{-\frac{E_a}{RT}} \implies A = e^2 B e^{\frac{\Delta^\ddagger S}{R}}; \quad \Delta^\ddagger S < 0$$

If there is reduction in entropy below what is expected for simple encounter of A+B, then A < value expected on the basis of simple collision theory

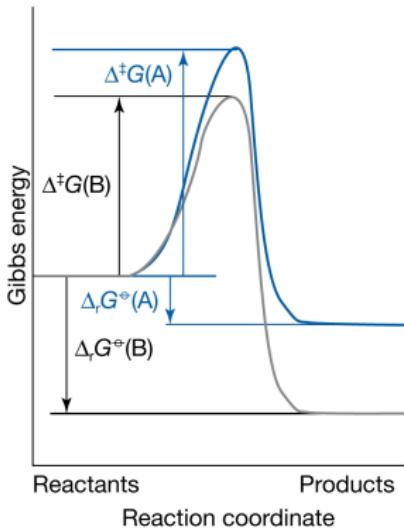
Additional reduction in entropy, $\Delta^\ddagger S_{\text{steric}}$ is the origin of steric factor of collision theory :

$$P = e^{\frac{\Delta^\ddagger S_{\text{steric}}}{R}}$$

The more complex the steric requirements of encounter, more negative is $\Delta^\ddagger S_{\text{steric}}$ and smaller is P

Gibbs energies, enthalpies, entropies, volumes, and heat capacities of **activation** are widely used to report experimental reaction rates, especially for organic reactions in solution

They are encountered when relationships between equilibrium constants and rates of reaction are explored using correlation analysis, in which $\ln K$ is plotted against $\ln k$



In many cases correlation is linear, signifying that, as reaction becomes thermodynamically more favourable, its rate constant increases

This linear correlation is the origin of alternative name - linear free energy relation

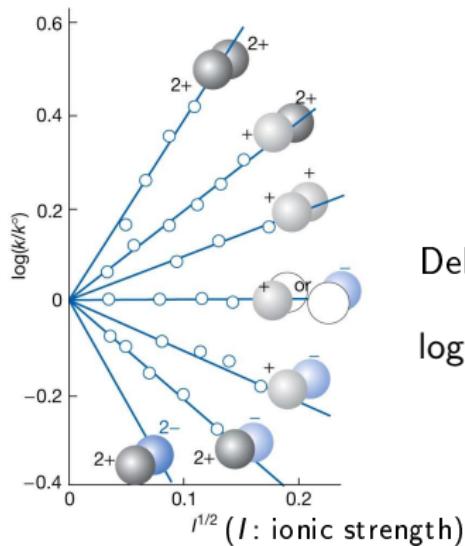
Reactions in solution : $K = \frac{a_C \cdot a_{C^\ddagger}}{a_A \cdot a_B} = K_\gamma \frac{[C^\ddagger]}{[A][B]} \quad K_\gamma = \frac{\gamma_{C^\ddagger}}{\gamma_A \gamma_B}$

$$\frac{d[P]}{dt} = k^\ddagger [C^\ddagger] = k_2 [A][B]$$

$$k_2 = \frac{k^\ddagger K}{K_\gamma}$$

If k_2^0 = rate constant when activity coeffs are 1,
i.e., $k_2^0 = k^\ddagger K$, then $k_2 = \frac{k_2^0}{K_\gamma}$

kinetic salt effect

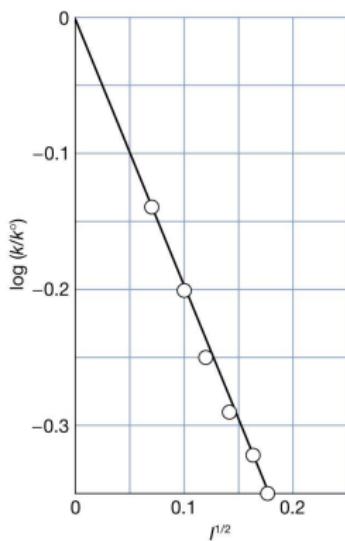


Debye Hückel: $\log \gamma_j = -A z_j^2 \sqrt{I}$

$$\begin{aligned} \log k_2 &= \log k_2^0 - A \left\{ z_A^2 + z_B^2 - (z_A + z_B)^2 \right\} \sqrt{I} \\ &= \log k_2^0 + 2A z_A z_B \sqrt{I} \end{aligned}$$

the base hydrolysis of $[\text{CoBr}(\text{NH}_3)_5]^{2+}$; task : charge on activated complex?

I	0.0050	0.0100	0.0150	0.0200	0.0250	0.0300
k/k°	0.718	0.631	0.562	0.515	0.475	0.447
$I^{1/2}$		0.071	0.100	0.122	0.141	0.158
$\log(k/k^\circ)$		-0.14	-0.20	-0.25	-0.29	-0.32



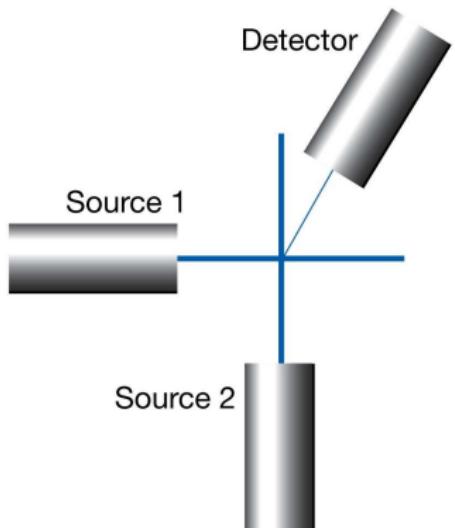
$$\text{slope} = -2.04 \implies z_A z_B = -2$$

$$\therefore z_A = -1 \text{ for } \text{OH}^- \implies z_B = 2 \implies$$

$[\text{CoBr}(\text{NH}_3)_5]^{+2}$ participates in the formation of activated complex

Molecular beams : collimated, narrow stream of molecules travelling though an evacuated vessel

Beam directed towards other molecules, scattering on impact is related to intermolecular interactions



study collisions between molecules in preselected energy states

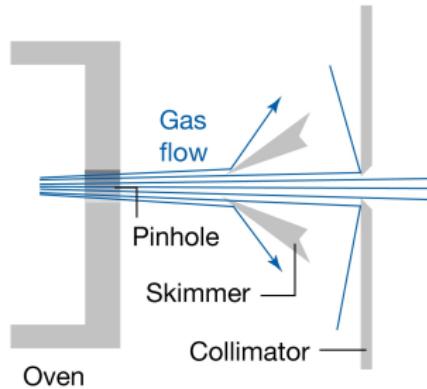
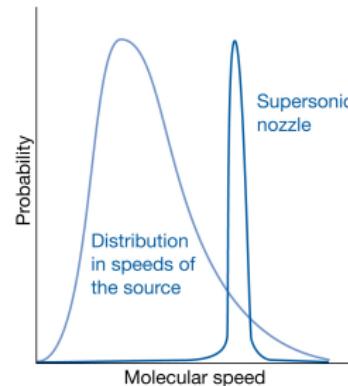
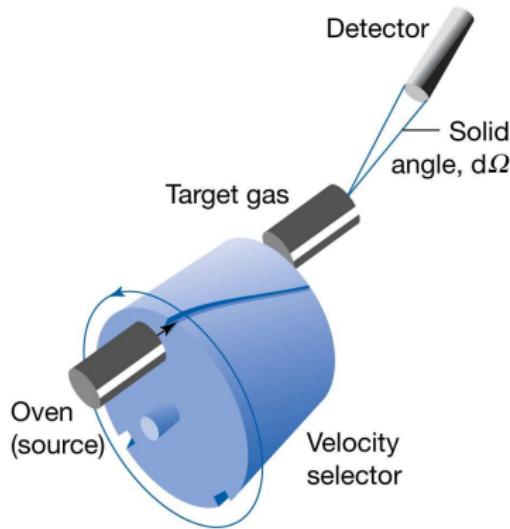
used to determine states of products of reactive collision.

rate constant is an average over events in which reactants in different initial states evolve into products in their final states

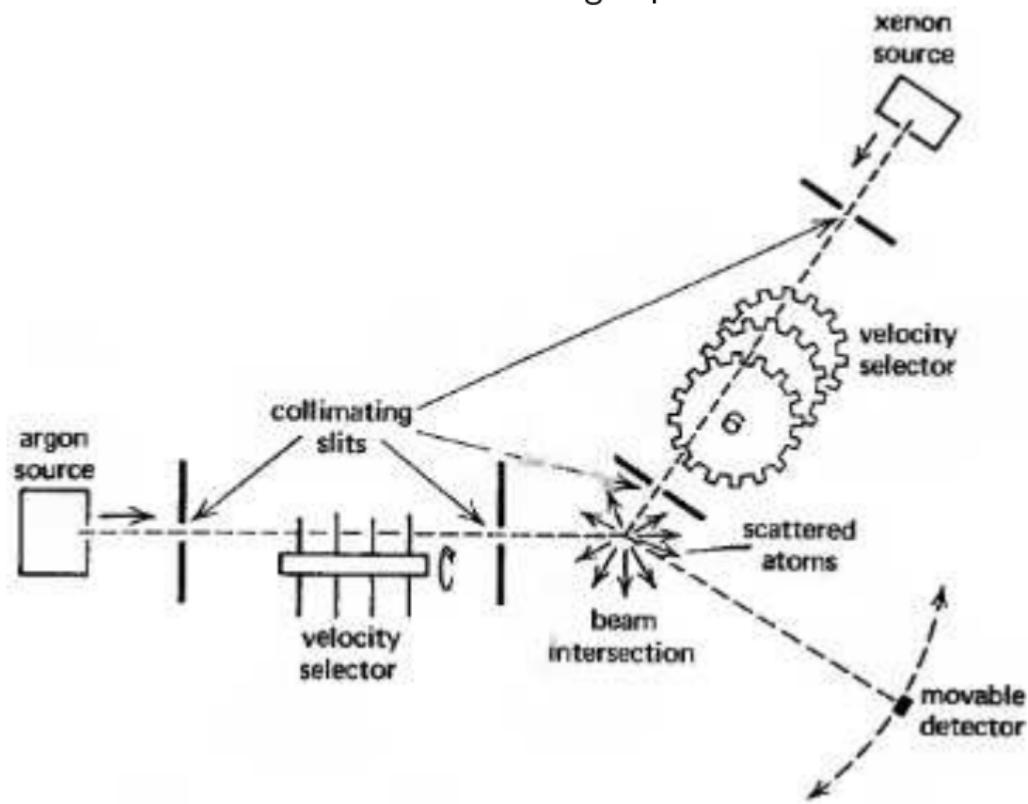
crossed-beam experiments

state-selected molecules are generated in two separate sources, and directed perpendicular to one another.

Detector responds to molecules (product if chemical reaction occurs) scattered into chosen direction



schematic of a Ar-Ne beam scattering experiment



Kinematics : collision between two point particles

masses : m_1 and m_2 ;

position coordinates : \vec{r}_1 and \vec{r}_2 (before) and \vec{r}'_1 and \vec{r}'_2 (after)

velocities : $\vec{v}_1 = \dot{\vec{r}}_1$ and $\vec{v}_2 = \dot{\vec{r}}_2$ (before) and $\vec{v}'_1 = \dot{\vec{r}}'_1$ and $\vec{v}'_2 = \dot{\vec{r}}'_2$ (after)

	momentum	energy
conservation :	$m_1 \vec{v}_1 + m_2 \vec{v}_2 = m_1 \vec{v}'_1 + m_2 \vec{v}'_2$	$m_1 \vec{v}_1^2 + m_2 \vec{v}_2^2 = m_1 \vec{v}'_1^2 + m_2 \vec{v}'_2^2$

	on particle 1 by particle 2	on particle 2 by particle 1
force exerted	$\vec{F}_1 = m_1 \frac{d^2 \dot{\vec{r}}_1}{dt^2}$	$\vec{F}_2 = m_2 \frac{d^2 \dot{\vec{r}}_2}{dt^2}$

Newton's 3rd law : $\vec{F}_1 = -\vec{F}_2$

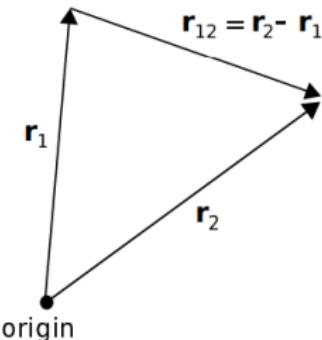
$$\therefore \frac{d^2 \dot{\vec{r}}_2}{dt^2} - \frac{d^2 \dot{\vec{r}}_1}{dt^2} = \frac{d}{dt} \left(\frac{d \dot{\vec{r}}_2}{dt} - \frac{d \dot{\vec{r}}_1}{dt} \right) = \left(\frac{1}{m_2} + \frac{1}{m_1} \right) \vec{F}_2 = \frac{\vec{F}_2}{\mu}$$

transformation of the two body problem into motion of a single particle in a field of force

relative position vector : $\vec{r} = \vec{r}_2 - \vec{r}_1$

relative velocity vector : $\vec{v} = \vec{v}_2 - \vec{v}_1$

$\mu \frac{d\vec{v}}{dt} = \vec{F}$ = force between particles 1 and 2



Eqn. of motion of a single particle of mass μ in field of force \vec{F}

C.M. motion : $M\vec{v}_{CM} = m_1\vec{v}_1 + m_2\vec{v}_2$; $M = m_1 + m_2$

transformation : $\begin{pmatrix} \vec{v}_{CM} \\ \vec{v} \end{pmatrix} = \begin{pmatrix} \frac{m_1}{M} & \frac{m_2}{M} \\ -1 & 1 \end{pmatrix} \begin{pmatrix} \vec{v}_1 \\ \vec{v}_2 \end{pmatrix}$

$$K.E. : \frac{1}{2}m_1\vec{v}_1^2 + \frac{1}{2}m_2\vec{v}_2^2 = \frac{1}{2}\mu\vec{v}^2 + \frac{1}{2}M\vec{v}_{CM}^2$$

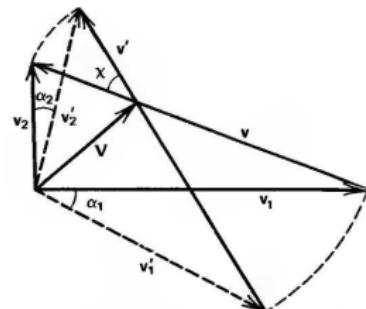
$\therefore \vec{v}_{CM}$ does not change in a collision (unless external forces exist)

\therefore Neglect CM motion

relative K.E. conserved : $\mu \vec{v}^2 = \mu \vec{v}'^2$

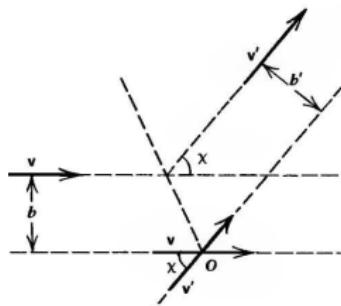
elastic collision :

magnitude of relative velocity invariant
particle 1 scattered through lab angle α_1



center of force representation

relative velocity
before and after collision



initially, fictitious particle with mass μ and velocity \vec{v} moves toward a center of force located at O

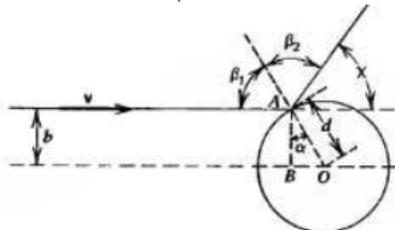
It may be pulled toward O by attractive forces or pushed away by repulsive forces

net effect : deflection of relative velocity vector \vec{v} into \vec{v}' through an angle χ : **scattering angle**

If no forces of interaction, fictitious particle passes by point O in a straight line
 b = impact parameter = \perp distance between particle trajectories

Hard sphere collisions :

diameter d , mass m



if $b > d$, no collision

▶ until very instant of impact \exists no forces

∴ they travel in straight lines

after (instantaneous) collision,

trajectory is again linear

▶ $\beta_1 + \beta_2 + \chi = \pi$ and

time reversal symmetry $\Rightarrow \beta_1 = \beta_2 = \frac{\pi - \chi}{2}$

$\therefore \alpha + \frac{\pi}{2} + \beta_1 = \pi, \therefore \alpha = \frac{\chi}{2}$

▶ for $b \leq d$, $b = d \cos \alpha = d \cos \frac{\chi}{2}$

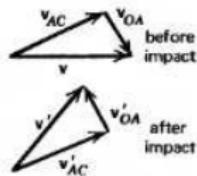
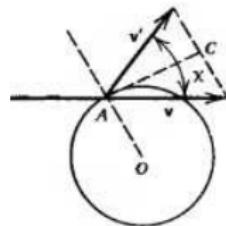
▶ if $b = 0$, head on collision, $\chi = \pi$

(and at instant of impact, $\vec{v}_{OA} = 0$, its contribution to KE is converted entirely into PE)

$\forall b \neq 0$, KE at instant of

$$\text{impact} = \dot{\vec{r}} = \vec{v}_{OA} = \frac{1}{2} \mu v^2 \cos^2 \frac{\chi}{2}$$

$$\text{PE at impact} = \frac{1}{2} \mu v^2 \left(1 - \cos^2 \frac{\chi}{2}\right) = \frac{1}{2} \mu v^2 \sin^2 \frac{\chi}{2}$$



$$\sigma(\theta) = \frac{\text{\#interactions per target particle leading to scattering into } d\Omega \text{ at angle } \theta}{\text{\#incident particles per unit area}}$$

$$\sigma(\theta) d\Omega = \frac{dN}{I} [\text{Note: more correctly, } \sigma(\theta) d\Omega \text{ should be written as } \frac{d\sigma}{d\Omega} d\Omega \text{ - a differential quantity and } \sigma = \int \frac{d\sigma}{d\Omega} d\Omega]$$

intensity (or flux density) I of incident particles

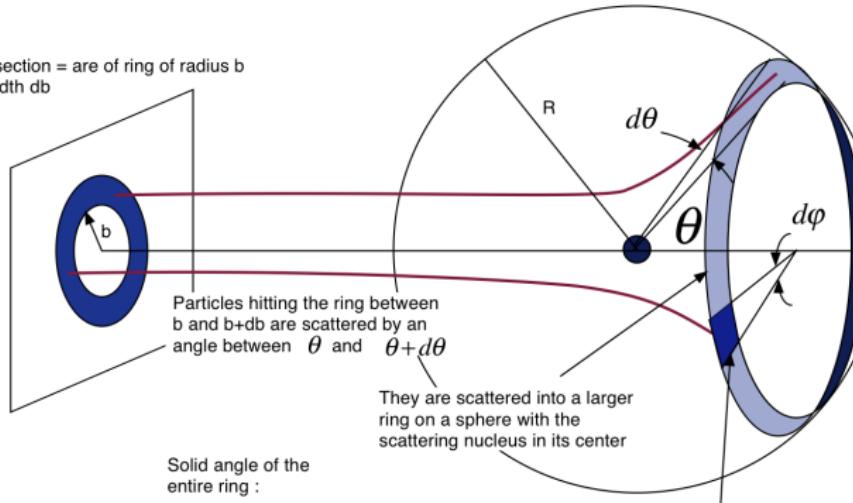
$= \#$ particles passing in unit time through unit area normal to beam

$dN = \#$ particles scattered into $d\Omega$ in unit time

Alternatively, $\frac{d\sigma}{d\Omega} = \frac{1}{I} \frac{dN}{d\Omega}$: dimensions of area per steradian

If scattering has axial symmetry (e.g., central forces)
 integrate over azimuthal angle to obtain 2π

cross section = area of ring of radius b
 and width db

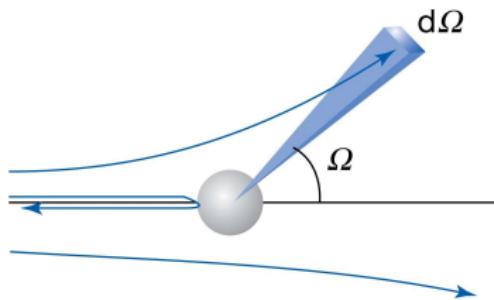


$$d\Omega = \frac{2\pi R \sin(\theta) R d\theta}{R^2} = 2\pi \sin(\theta) d\theta$$

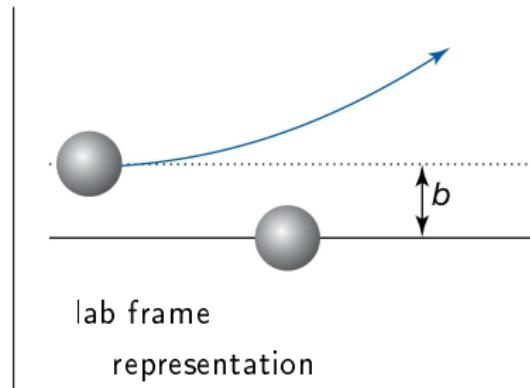
solid angle of small area:

$$d\Omega = \frac{d\varphi R \sin(\theta) R d\theta}{R^2} = \sin(\theta) d\theta d\varphi$$

and then element of solid angle $d\Omega = 2\pi \sin \theta d\theta$

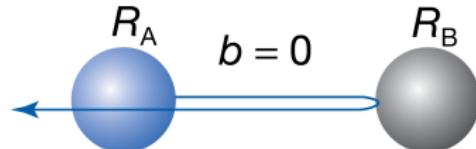


center of force representation

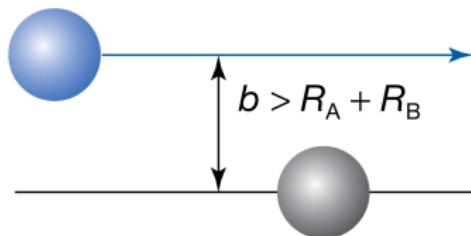


lab frame
representation

Differential cross-section, depends on the impact parameter, b and details of intermolecular potential

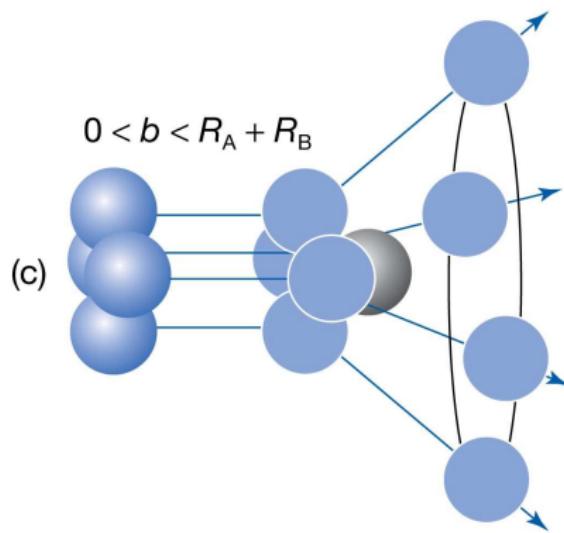


lighter projectile on a trajectory that leads to a head-on collision :
only scattering intensity detected when detector is
at $\theta = \pi$.

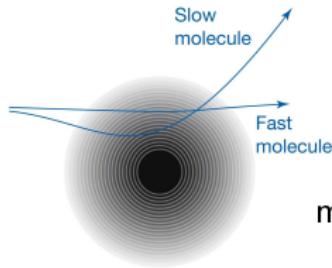


no scattering and $\sigma = 0$ at all angles
except $\theta = 0$

Glancing blows, with $0 < b \leq R_A + R_B$ lead to scattering intensity in cones around forward direction



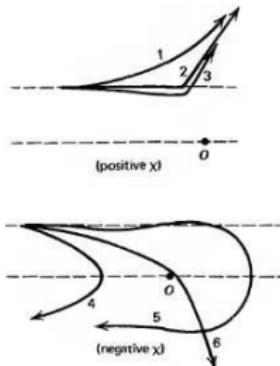
scattering pattern of real molecules (soft spheres) depends on details of intermolecular potential, including anisotropy when molecules are non-spherical



it also depends on relative speed of approach of particles

a very fast particle may pass through interaction region without much deflection, whereas a slower one may be temporarily captured and undergo considerable deflection

∴ variation of scattering cross-section with relative speed should give information about strength and range of intermolecular potential



1. purely repulsive
2. hard-sphere
- 3,4,5. attractive at large distances, repulsive at small
6. purely attractive

if $\chi = 0$: no collision $\Rightarrow V(d) = 0$

if $\chi = \pi$: head-on collision \Rightarrow

$$V(d) = \frac{1}{2}\mu v^2 = E, \text{ entire initial kinetic energy}$$

formulating shape of any particular trajectory :

fictitious particle of mass μ and initial velocity v impinges on a scattering center at O with impact parameter b

and is scattered at an angle χ

relative motion must

stay in the plane, as
there are no forces to
push particle out of
the plane

\therefore two coordinates,
 R and θ , suffice to
describe particle
position



PE at point of closest approach ($R_0 \equiv d$)

or energy along line of centers, $V(d) = E \left(1 - \frac{b^2}{d^2}\right)$

at $R = R_0$, $\theta = \frac{\pi - \chi}{2}$

$$KE = \frac{1}{2}\mu\dot{R}^2 + \frac{1}{2}\mu R^2\dot{\theta}^2$$

total energy = initial KE

$$E = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu\dot{R}^2 + \frac{1}{2}\mu R^2\dot{\theta}^2 + V(R)$$

ang. mom, $L = \mu v b = \mu R^2 \dot{\theta}$ or, $\dot{\theta} = \frac{vb}{R^2}$

$$\therefore E = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu\dot{R}^2 + \frac{1}{2}\mu v^2 \frac{b^2}{R^2} + V(R)$$

$$\dot{R} = \sqrt{v^2 - v^2 \frac{b^2}{R^2} - \frac{V(R)}{\frac{1}{2}\mu}}$$

$$\therefore \frac{d\theta}{dR} = \frac{\dot{\theta}}{\dot{R}} = \frac{b}{R^2 \sqrt{1 - \frac{b^2}{R^2} - \frac{V(R)}{E}}}$$

$$\text{At } R = R_0, \dot{R} = 0 \implies 1 - \frac{b^2}{R_0^2} = \frac{V(R_0)}{E}$$

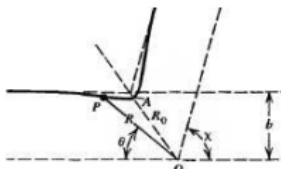
(R, θ) change from $(\infty, 0)$ to (R_0, θ_0) and then to $(\infty, \pi - \chi)$

\because trajectory is symmetric, we can integrate from $R = R_0 \rightarrow \infty$ and multiply the integral by 2 to get, scattering angle,

$$\chi = \pi - 2b \int_{R_0}^{\infty} \frac{dR}{R^2 \sqrt{1 - \frac{b^2}{R^2} - \frac{V(R)}{E}}}$$

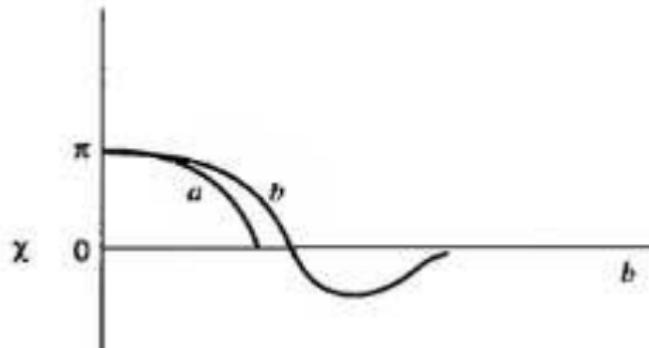
$$\text{hard sphere : } V(R) = \begin{cases} 0 & \forall R \geq d \\ \infty & \forall R < d \end{cases}$$

$$\chi = \pi - 2b \int_d^{\infty} \frac{dR}{R^2 \sqrt{1 - \frac{b^2}{R^2}}} = 2 \cos^{-1} \frac{b}{d} \quad \text{or, } b = d \cos \frac{\chi}{2}$$



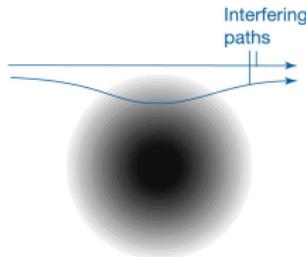
$$\frac{d\theta}{dR} = \frac{b}{R^2 \sqrt{1 - \frac{b^2}{R^2} - \frac{V(R)}{E}}}$$

Variation of the scattering angle vs. impact parameter



(a) hard- sphere potential, and (b) Lennard-Jones potential

Outcome of collisions determined by quantum, not classical, mechanics
particle with a certain impact parameter may approach attractive region of potential
and is deflected towards repulsive core, which then repels it out
through attractive region to continue flight in forward direction

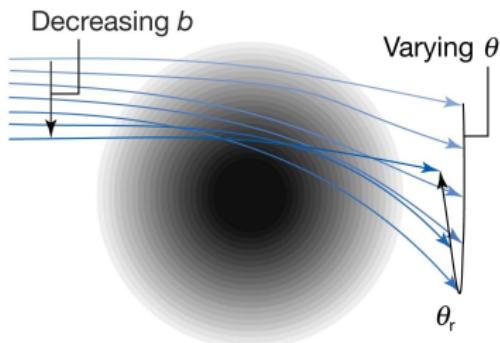


Some molecules also travel in forward direction because
they have impact parameters so large that they are
undeflected

wave functions of particles that take the two types of path interfere
and intensity in forward direction is modified \Rightarrow quantum oscillation
Same phenomenon accounts for the optical 'glory effect'

: bright halo seen surrounding an illuminated object

2nd quantum effect : strongly enhanced scattering in a non-forward direction \Rightarrow rainbow scattering because same mechanism accounts for the appearance of an optical rainbow

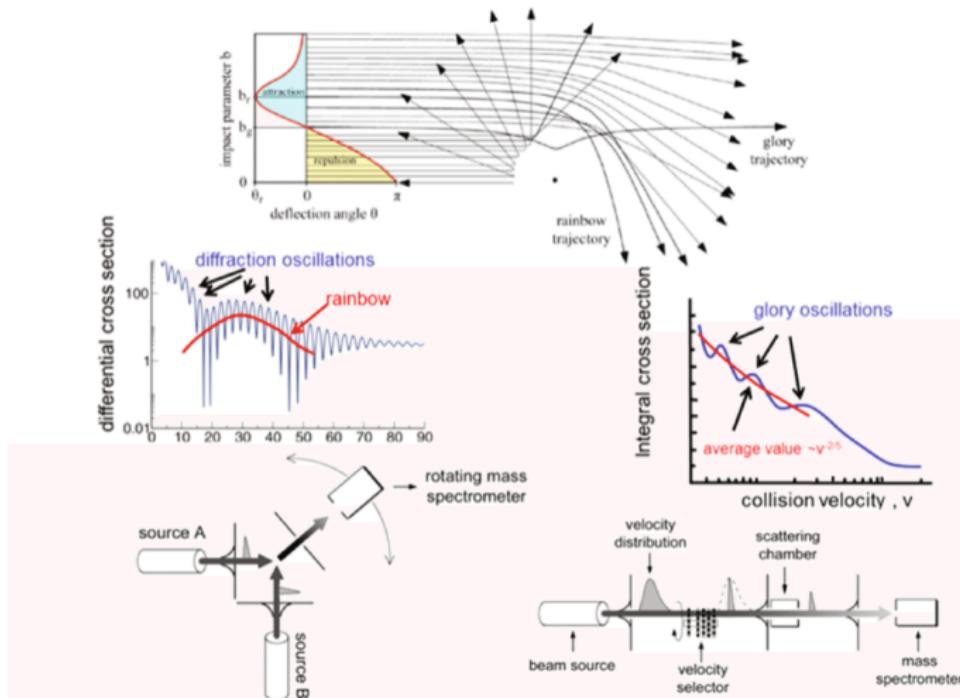


As impact parameter decreases, at one stage scattering angle passes through a maximum and interference between paths results in strongly scattered beam

$$1.2\pi.bdb = \frac{d\sigma}{d\Omega} 2\pi \sin \chi d\chi$$

rainbow angle, θ_r : $\frac{d\theta}{db} = 0$ and scattering is strong : $\frac{d\sigma}{d\Omega} = b \frac{1}{|\sin \chi \frac{d\chi}{db}|}$

elastic scattering



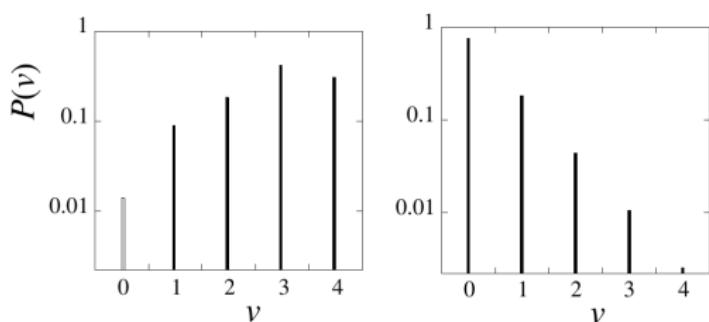
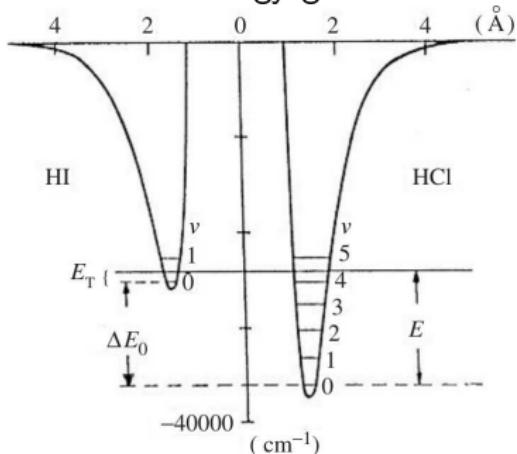
Another phenomenon that occurs in certain beams is capturing of one species by another

vibrational temperature in supersonic beams is so low that van der Waals molecules may be formed, which are complexes of the form AB in which A and B are held together by van der Waals forces or hydrogen bonds

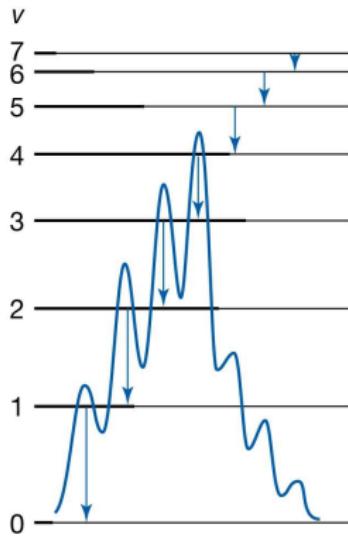
e.g., ArHCl, (HCl)₂, ArCO₂, and (H₂O)_n, (n = 2 – 6)

energy disposal in an exoergic reaction : $\text{Cl} + \text{HI} \rightarrow \text{ClH} + \text{I}$

relatively weak HI bond is broken and replaced by the stronger HCl bond. The reaction liberates chemical energy ($\sim 134\text{ kJ/mol}$) : where does the liberated energy go?



microscopic approach of molecular dynamics is concerned with outcome of individual reactive collisions



IR chemiluminescence from CO produced in the reaction $O + CS \rightarrow CO + S$ arises from non-equilibrium populations of vibrational states of CO and radiative relaxation to equilibrium

Other techniques:

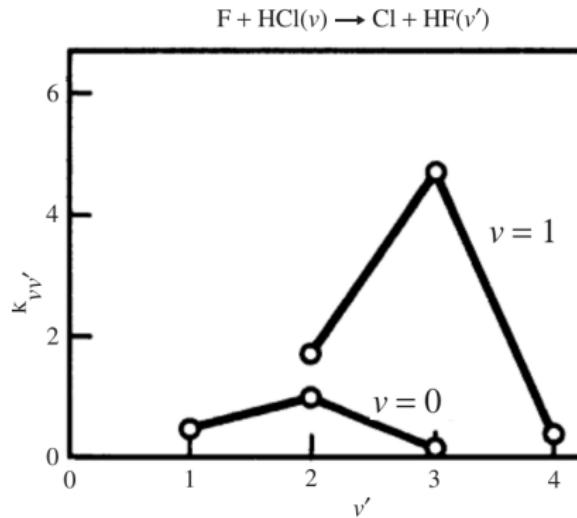
LIF

MPI

reaction product imaging

REMPI

Influence of the vibrational state of the reactant molecule
on distribution of vibrational states of product



effect of reagent vibration upon overall reaction rate :
reaction is \sim five times more efficient from $v = 1$ state

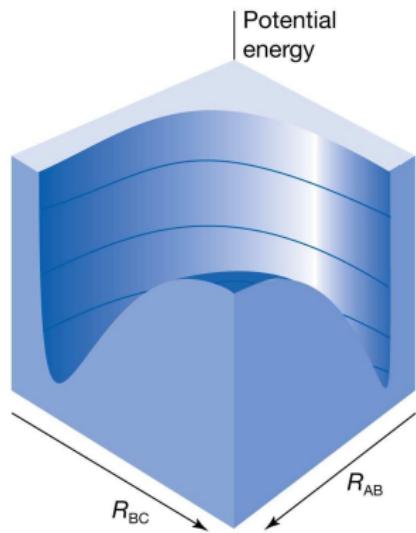
State-to-state dynamics

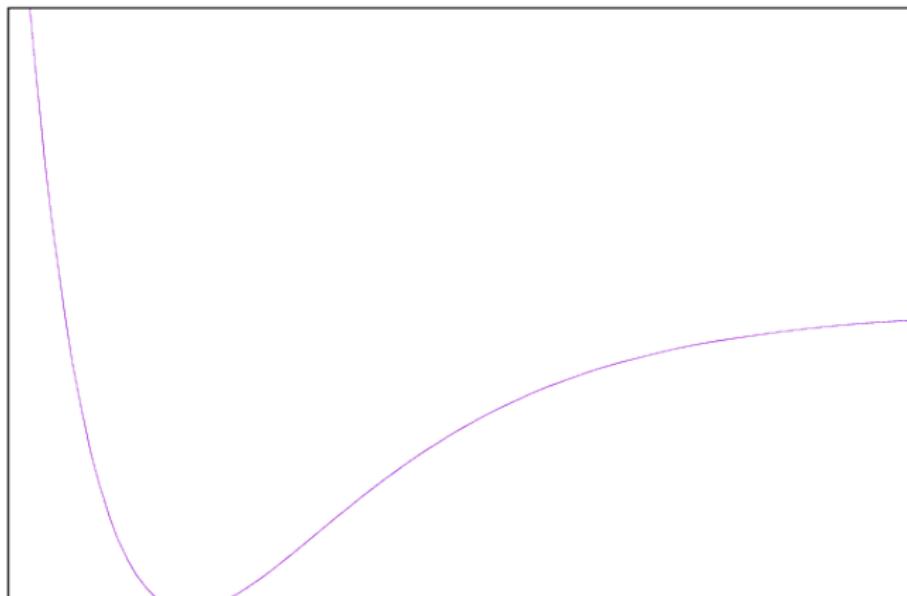
$$k_2 = \langle \sigma v_{rel} \rangle N_A$$

$$k_{n n'} = \langle \sigma_{n n'} v_{rel} \rangle N_A$$

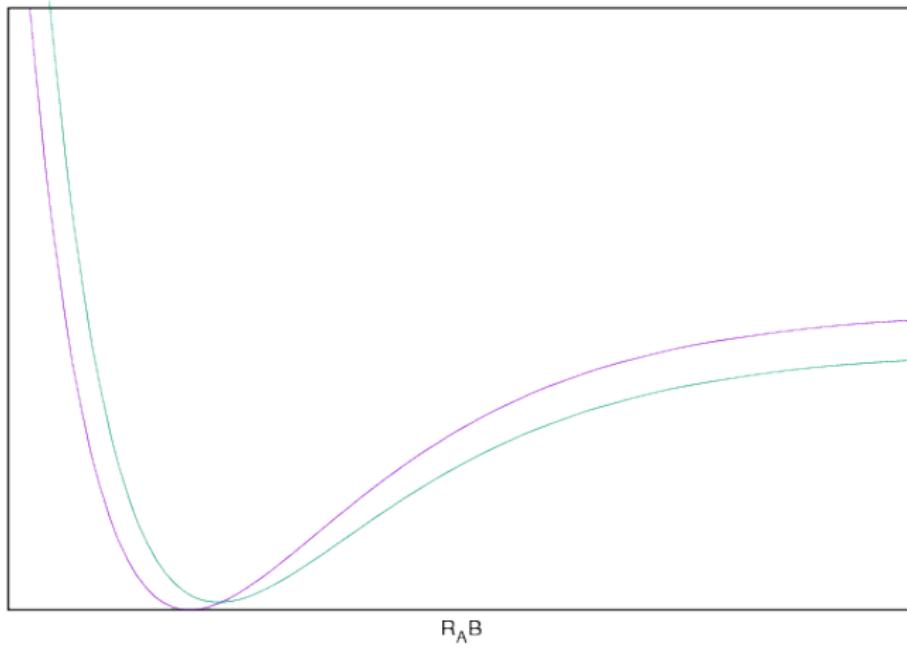
$$k_2 = \sum_{n n'} k_{n n'}(T) f_n(T)$$

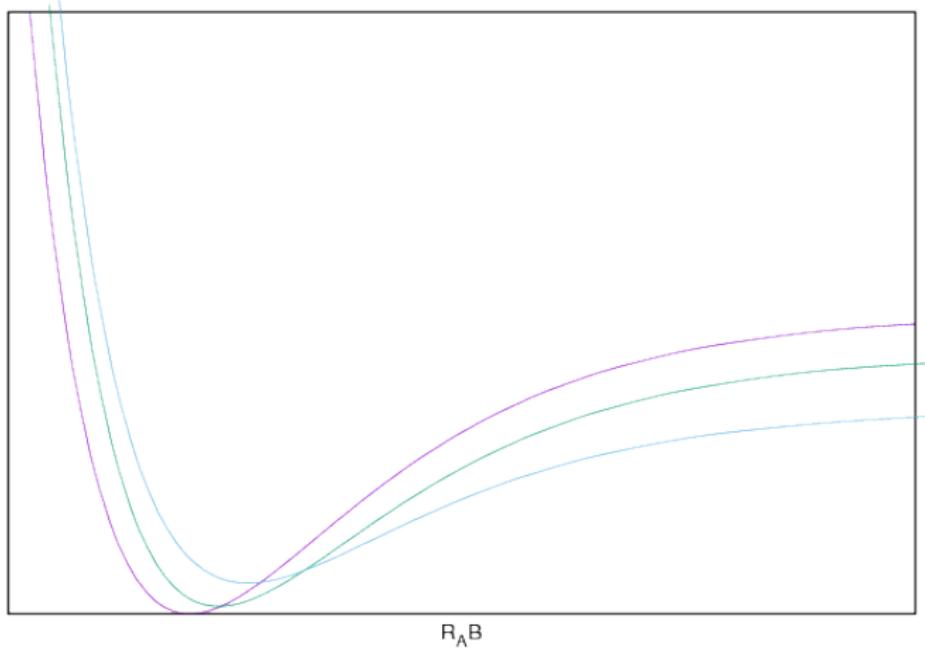
PES for the collinear $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction.

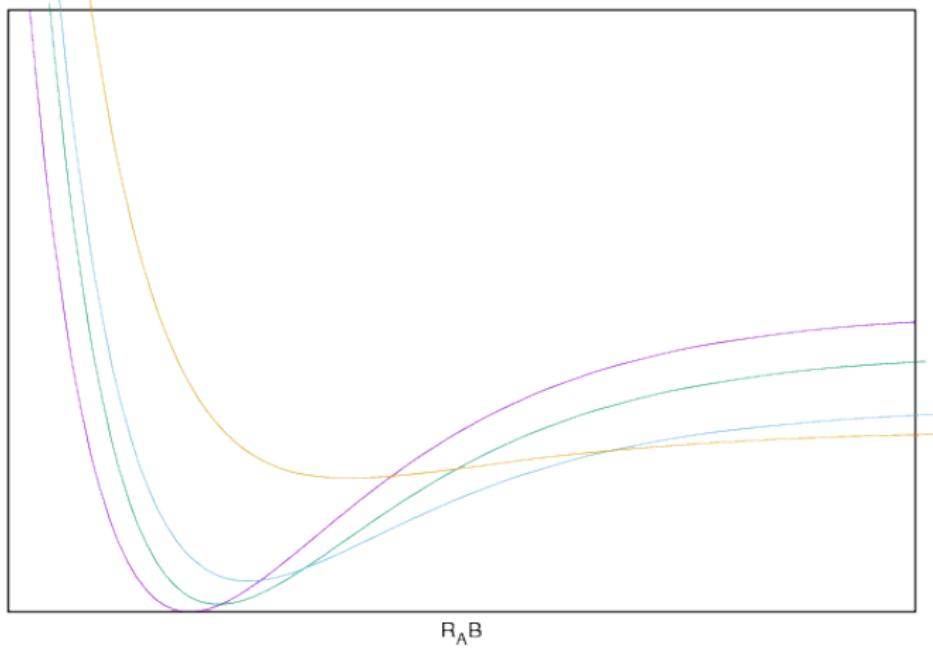


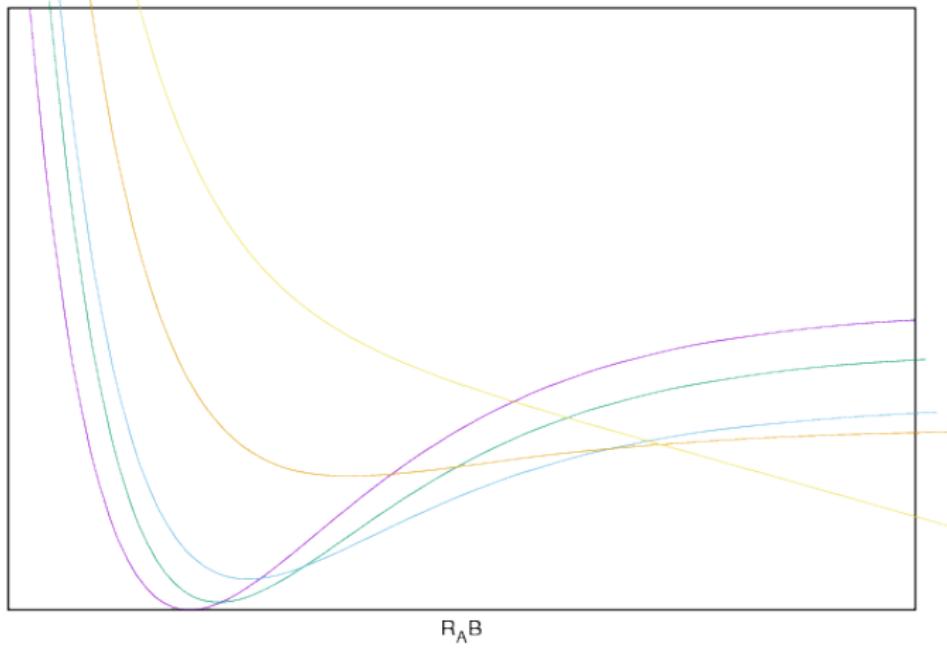


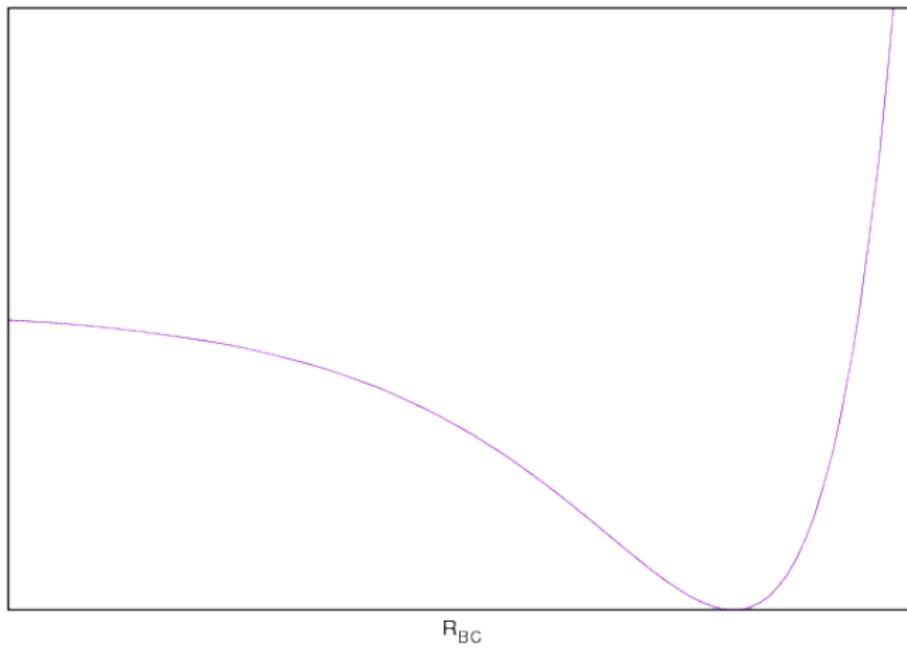
R_{AB}

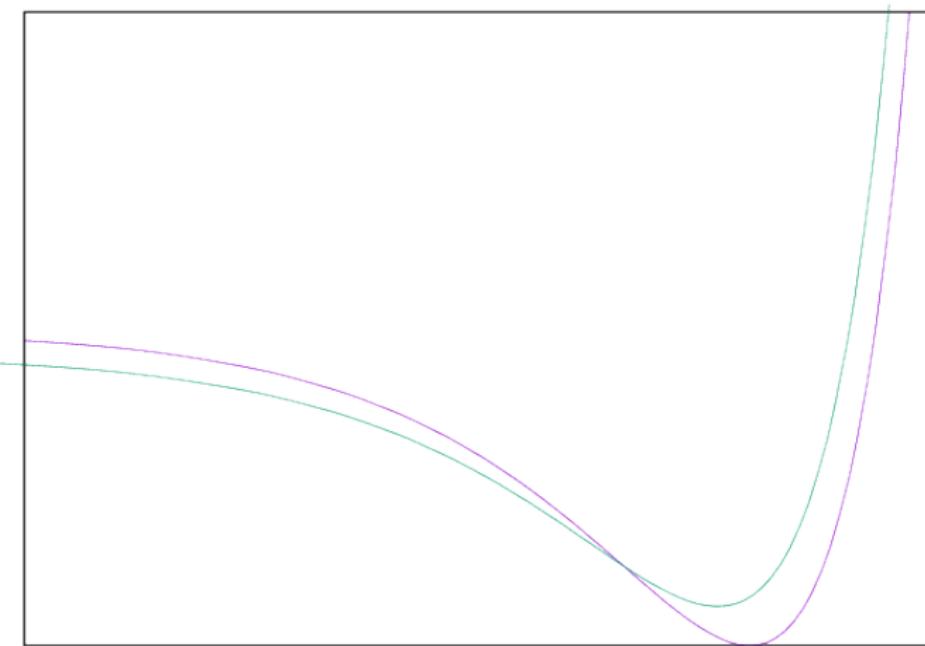


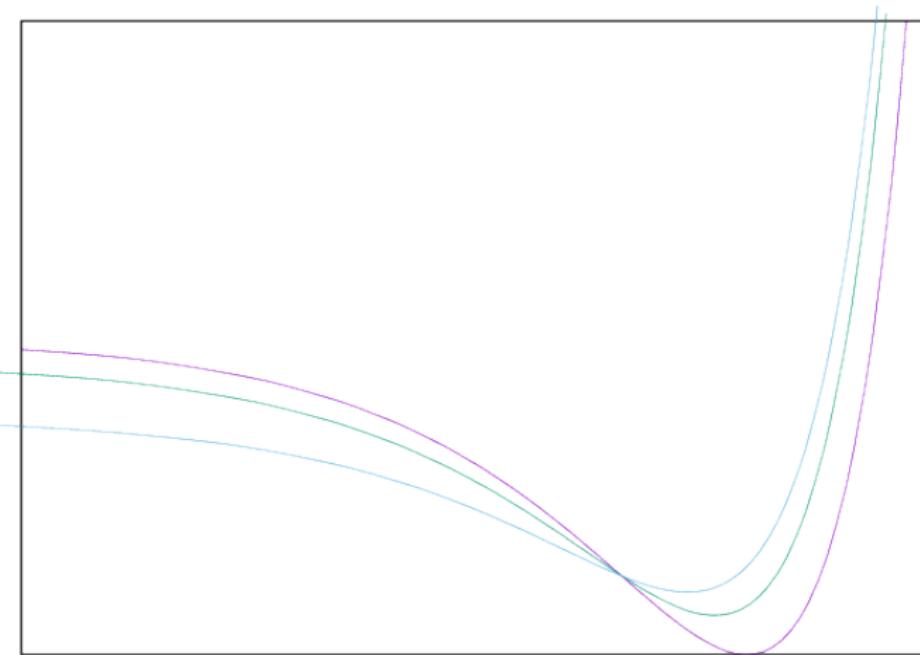


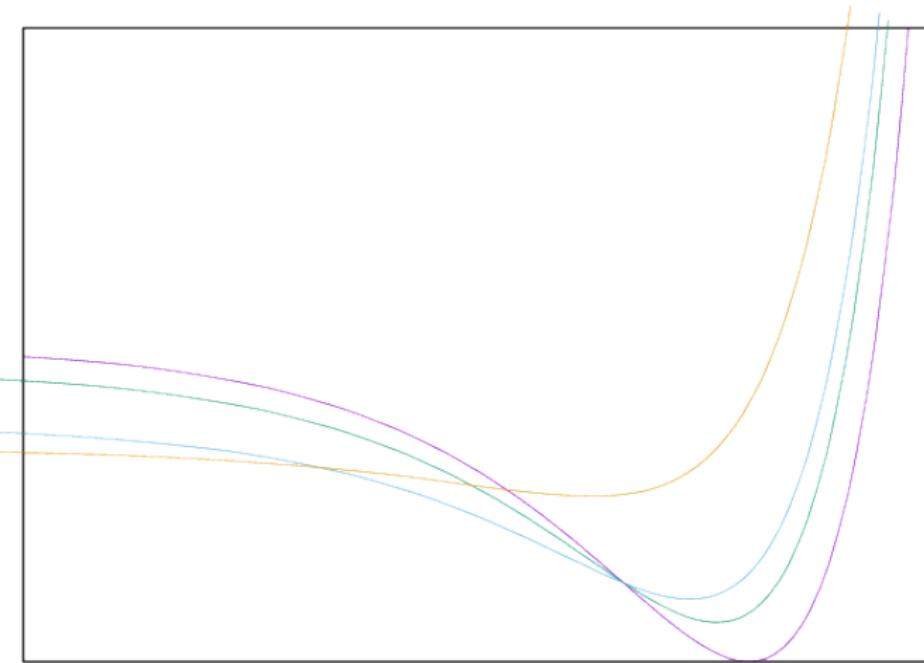


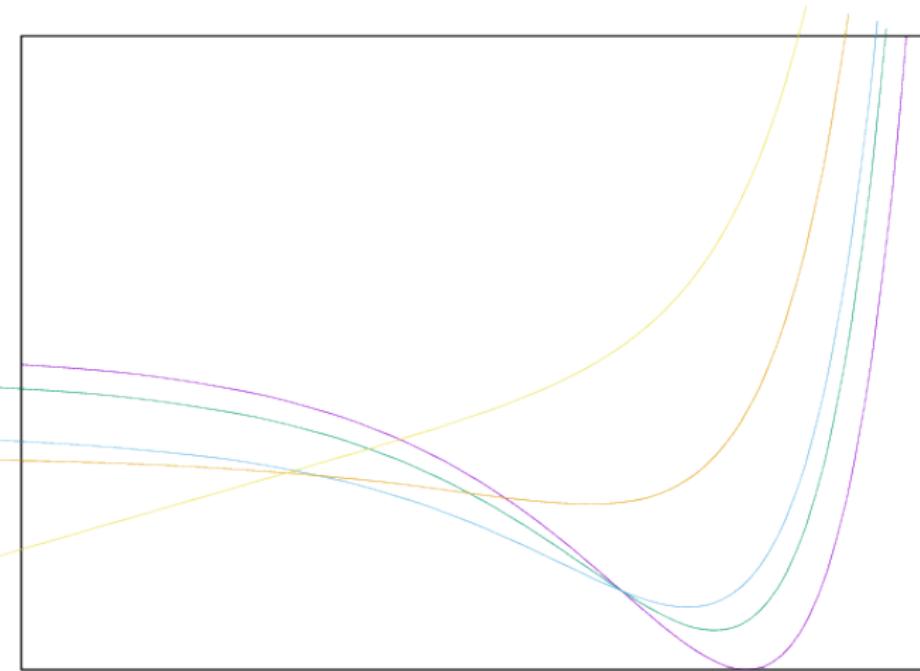


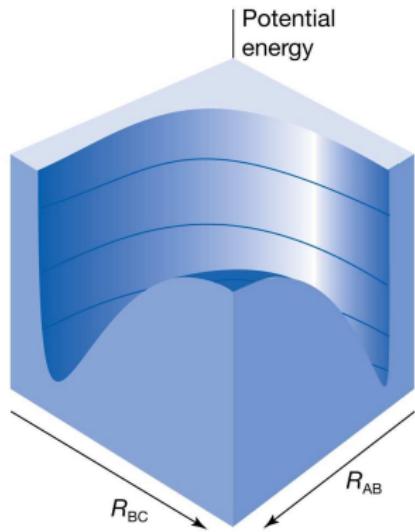


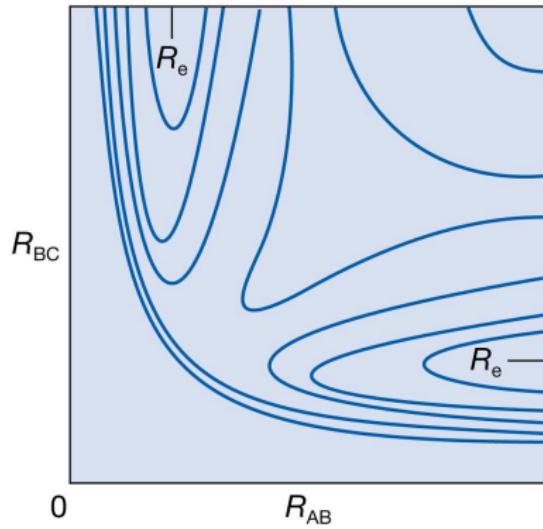


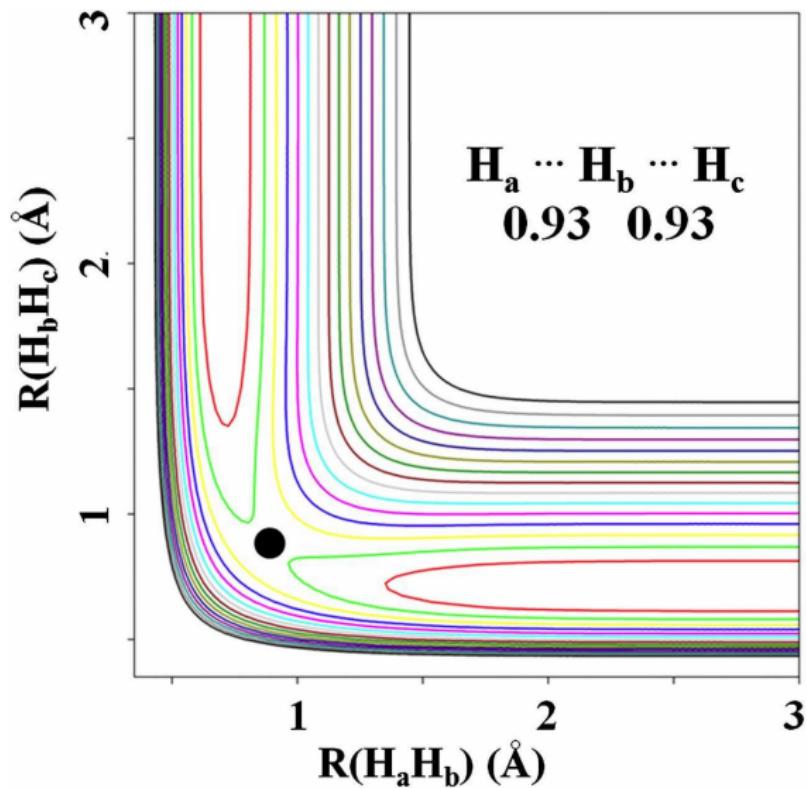


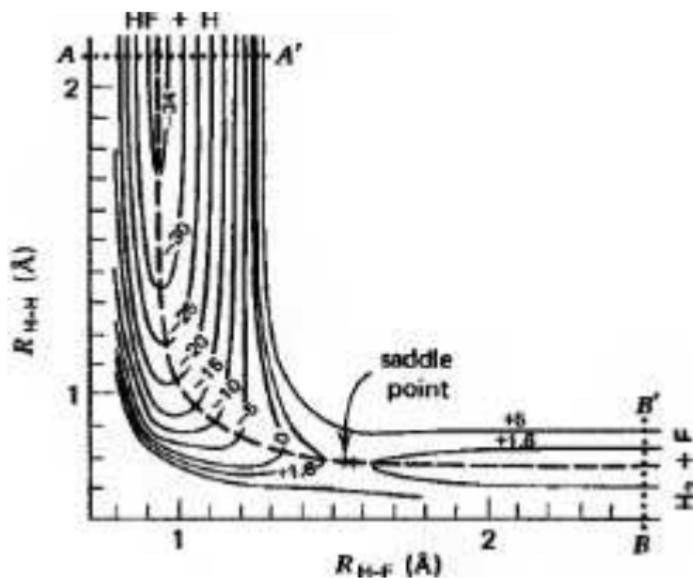


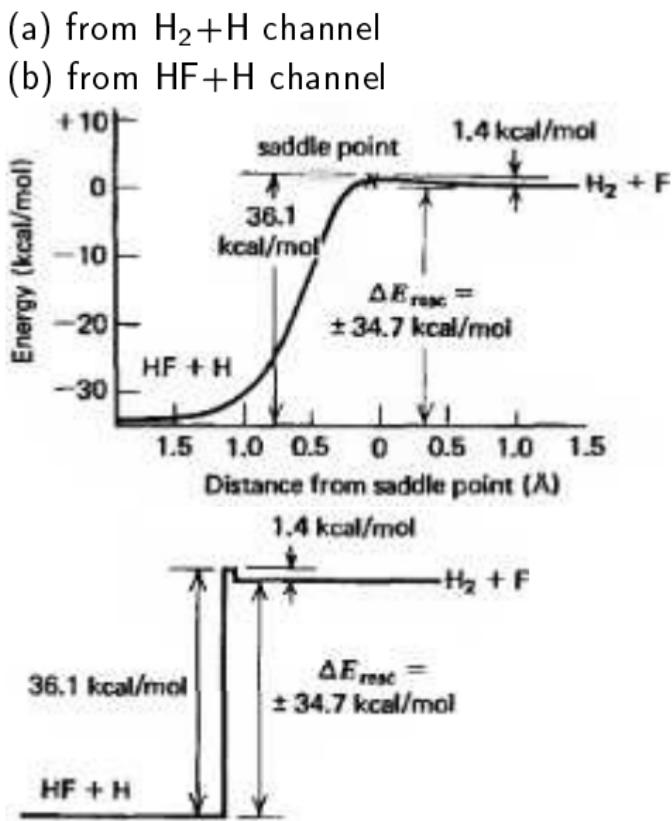
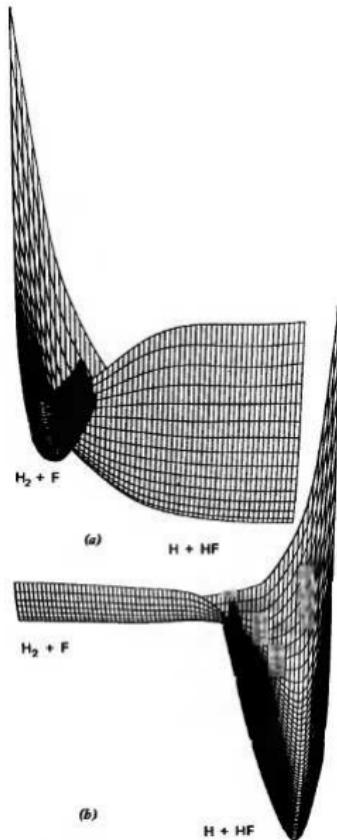




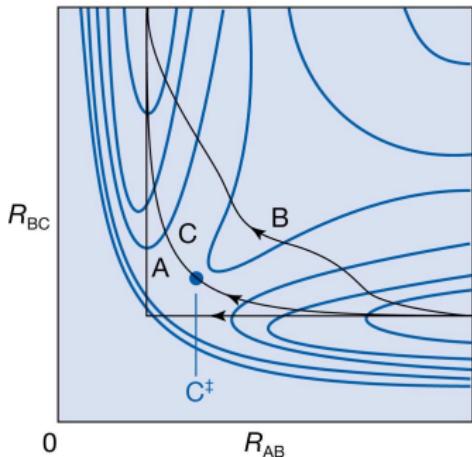








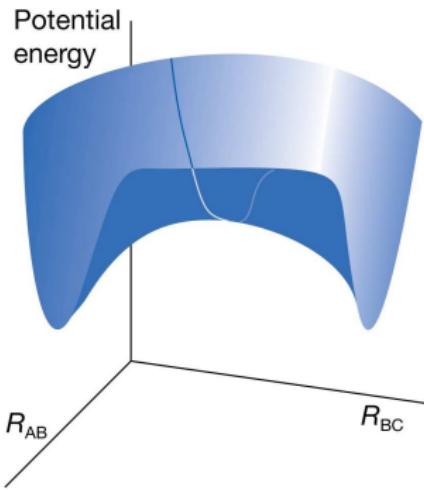
Trajectories through the potential energy surface



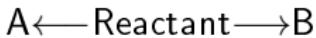
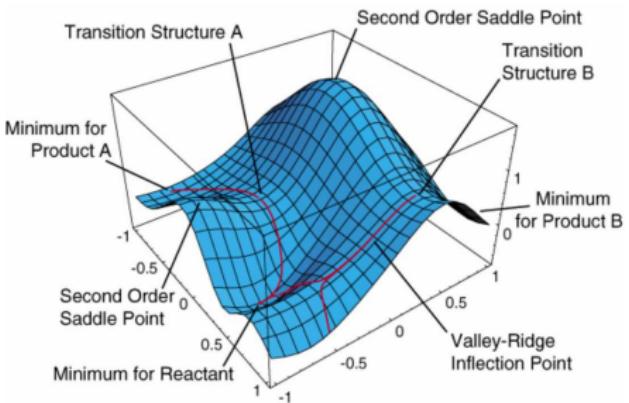
A : route in which R_{BC} is held constant as H_A approaches

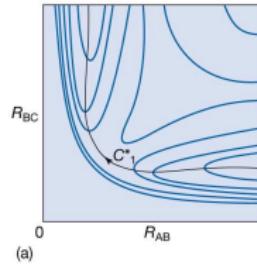
B : route in which R_{BC} lengthens at an early stage during the approach of H_A

C: route along the floor of the potential valley

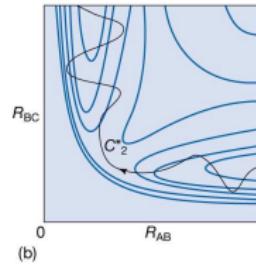


TS: set of configurations (marked by the line across saddle point) through which successful reactive trajectories must pass

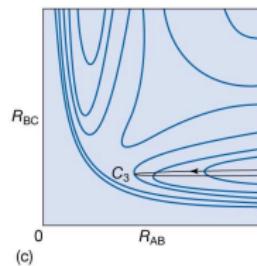




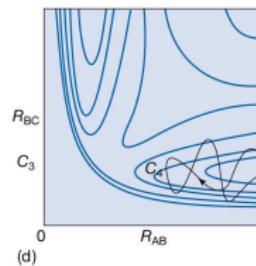
(a)



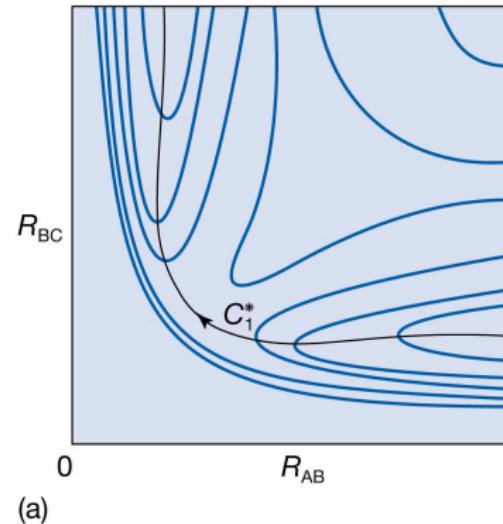
(b)



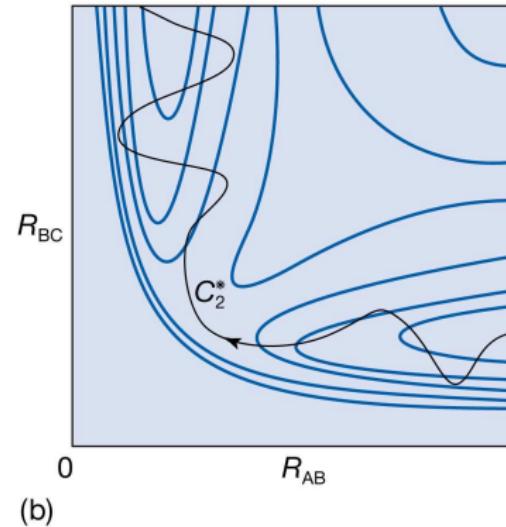
(c)



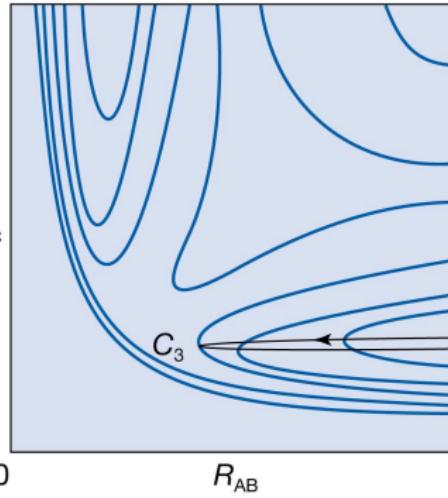
(d)



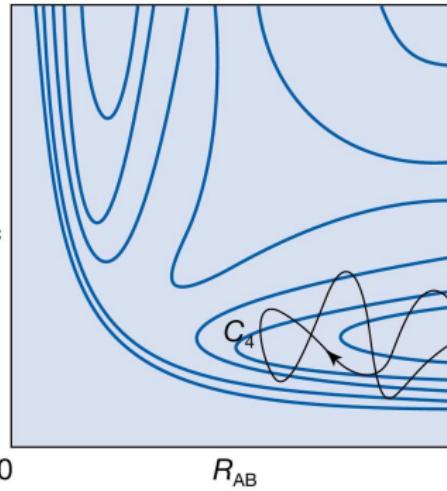
(a)



(b)

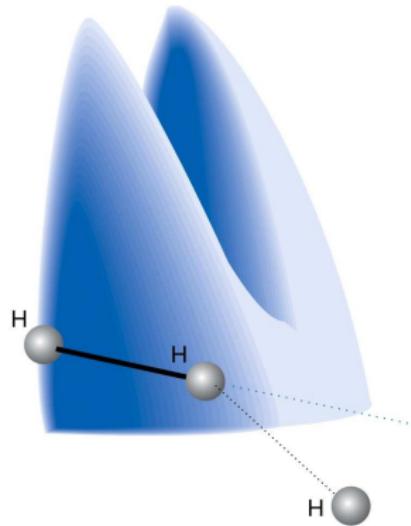


(c)

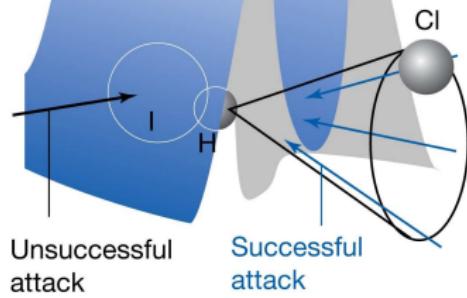
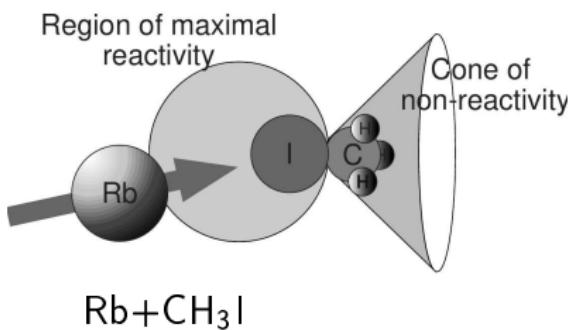


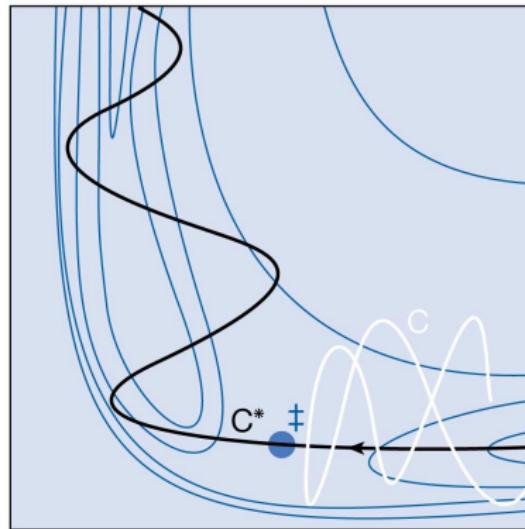
(d)

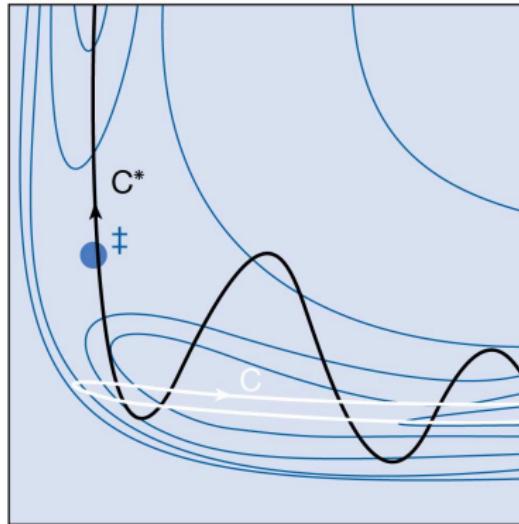
- ▶ attractive surface : in which saddle point occurs early in reaction coordinate
- ▶ repulsive surface : in which saddle point occurs late
- ▶ surface that is attractive in one direction is repulsive in the reverse direction

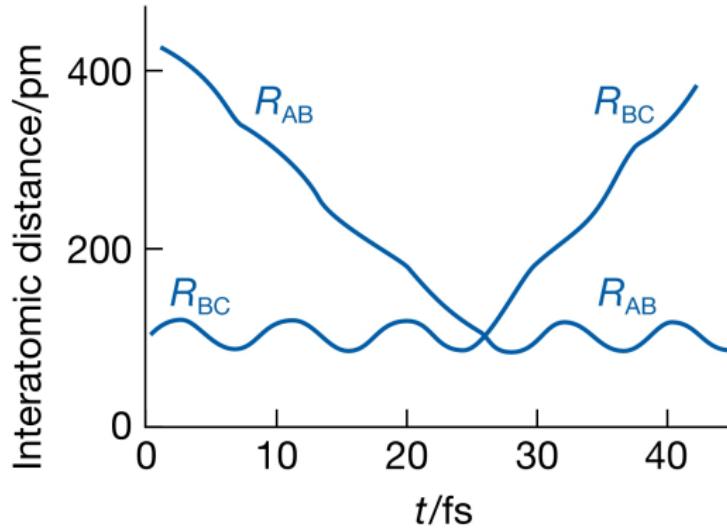


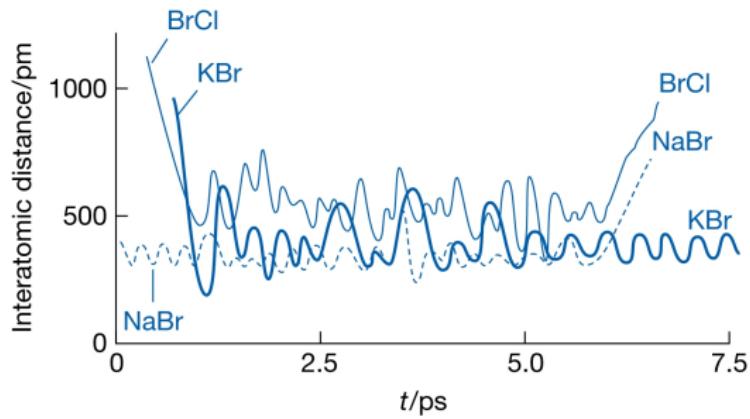
steric requirements









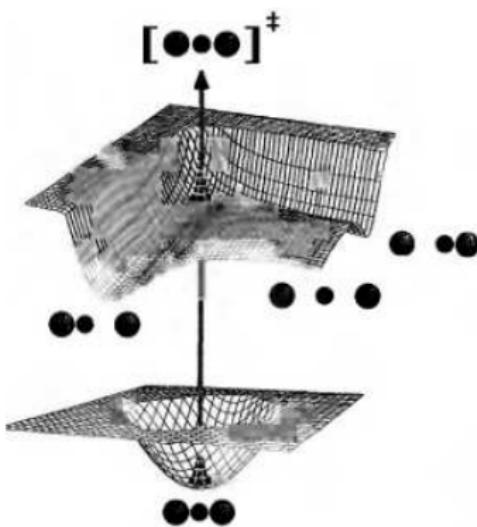


Femtochemistry

Most elementary steps into which any sequence of chemical reactions can be broken have a common time scale dictated by rapidity of nuclear rearrangement

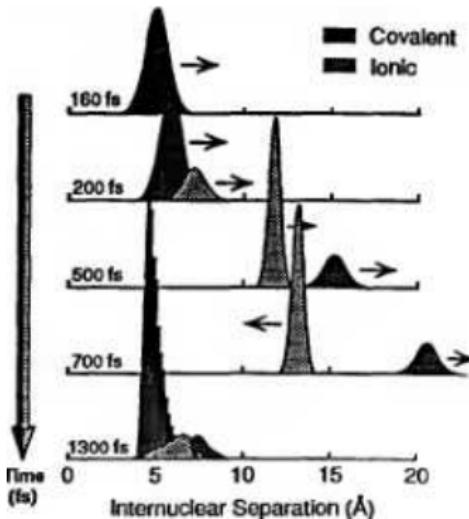
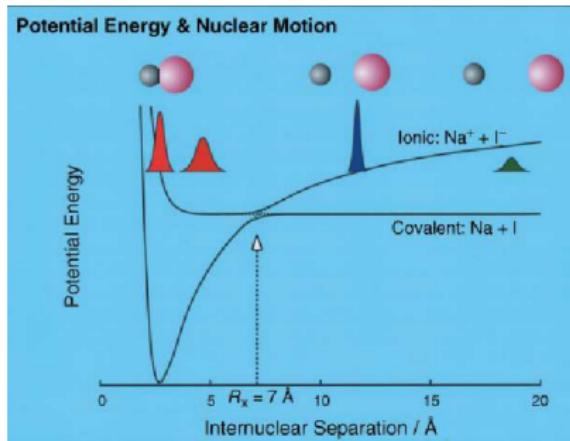
This fundamental chemical time scale ranges from 10fs and up

Femtochemistry deals with such dynamics of the chemical bond for an understanding of what happens in $10 - 10^4$ fs

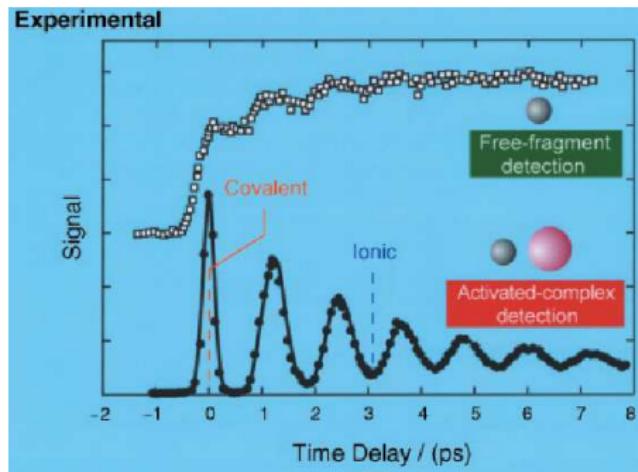
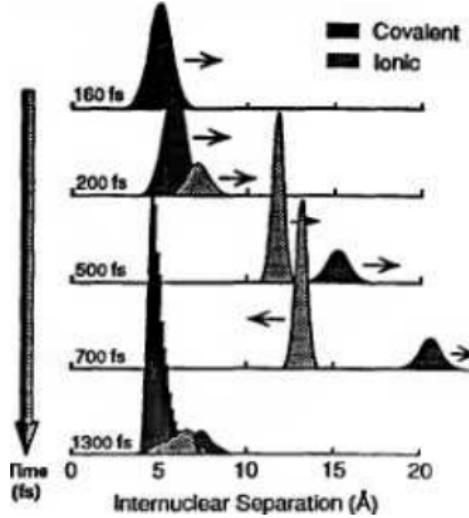


Promotion of a Gaussian wave packet by fs pump pulse of laser light from ground state of a molecule with 3 atoms ABA to transition state

From TS $[ABA]^\ddagger$, wave packet can proceed to
 $A + BA$ or $AB + A$

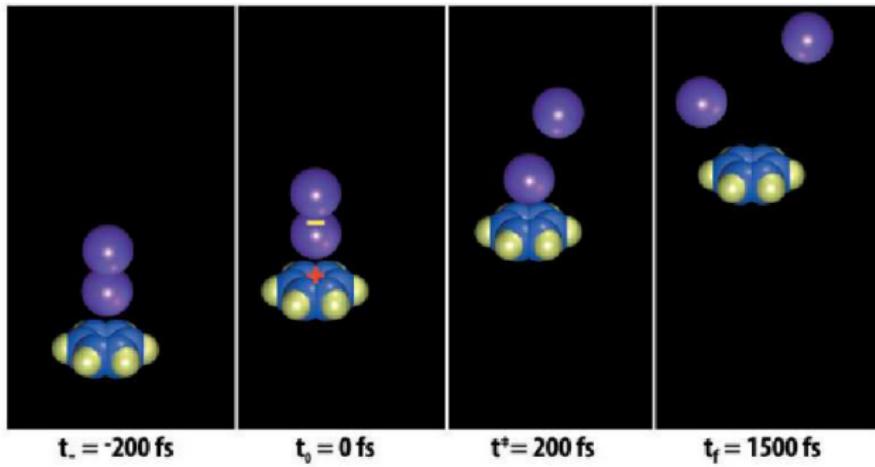


QM calculations : wavepacket motion



top: free Na

bottom: complex $[\text{Na} \dots \text{I}]^\dagger$ (oscillations)



reaction in progress involving two molecules (bimolecular)

I_2 is split by exchange of an electron with C_6H_6

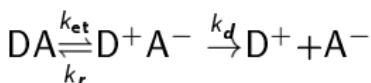
Electron transfer in homogeneous systems : $D + A \rightarrow D^+ + A^-$

$$v = k_{obs}[D][A];$$

$$K = \frac{[D^+][A^-]}{[D][A]}$$

first step : D and A diffuse through solution and collide to form complex DA

donor-acceptor separated by $\sim r$



$$\frac{d[D^+A^-]}{dt} = k_{et}[DA] - k_r[D^+A^-] - k_d[D^+A^-] = 0$$

$$[D^+A^-] = \frac{k_{et}}{k_r + k_d} [DA]$$

$$\frac{d[DA]}{dt} = k_a[D][A] - k'_a[DA] - k_{et}[DA] + k_r[D^+A^-] = 0$$

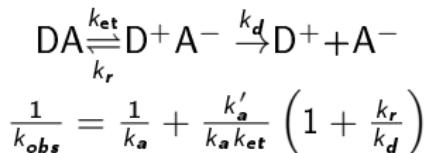
$$\begin{aligned} \text{or, } (k'_a + k_{et})[DA] &= k_a[D][A] + k_r[D^+A^-] \\ &= k_a[D][A] + \frac{k_r k_{et}}{k_r + k_d} [DA] \end{aligned}$$

$$\text{or, } [DA] = \frac{k_a(k_r + k_d)}{k'_a k_r + k'_a k_d + k_d k_{et}} [D][A]$$

$$\therefore [D^+A^-] = \frac{k_a k_{et}}{k'_a k_r + k'_a k_d + k_d k_{et}} [D][A]$$

$$\therefore v = k_d[D^+A^-] = k_{obs}[D][A] = \frac{k_d k_a k_{et}}{k'_a k_r + k'_a k_d + k_d k_{et}} [D][A]$$

$$\text{and } k_{obs} = \frac{k_d k_a k_{et}}{k'_a k_r + k'_a k_d + k_d k_{et}} \implies \frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{k'_a}{k_a k_{et}} \left(1 + \frac{k_r}{k_d}\right)$$



- For $k_d \gg k_r$, $\frac{1}{k_{obs}} = \frac{1}{k_a} \left(1 + \frac{k'_a}{k_{et}} \right)$
- if $k_{et} \gg k'_a$, $k_{obs} \approx k_a$; diffusion controlled
- fosters formation of DA complex
- if $k_{et} \ll k'_a$, $k_{obs} \approx \frac{k_a}{k'_a} k_{et} = K_{DA} k_{et}$; process controlled by activation
- TST: $k_{et} = \kappa \nu e^{-\frac{\Delta_f^{\ddagger} G}{RT}}$

Electron transfer reactions are ubiquitous

ex. : redox reactions in solution, $A \text{ (red)} + B \text{ (ox)} \rightarrow A \text{ (ox)} + B \text{ (red)}$

When one of these reactants B is an electrode M, we have electrochemical reaction: $A \text{ (red)} + M \rightarrow A \text{ (ox)} + M(e)$

ET occur for inorganic systems and organic ones
for reactions in solution and for those across interfaces
in complex biological systems and in very simple systems

ex. : self-exchange reaction



Experimentally rates of such reactions were initially measured for a wide variety of central metal atoms and ligands (here, Mn and O, respectively) by labeling one of the metal atoms in a particular valence state with a radioactive atom as a tracer and following its appearance in the other valence state

Central idea underlying ET can be illustrated using above reaction

When electron jumps from the MnO_4^{2-} to MnO_4^-

it does it so rapidly that atoms in the reactants and solvent molecules do not have time to move in the brief instant, as atoms are much heavier than electron
i.e., the transfer should obey Franck-Condon principle

This constraint has major consequences

solvent dipolar molecules are partially oriented, on average, towards ions, and much more so toward the more highly charged ion

∴ each of the newly formed ions suddenly finds itself in a wrong solvent environment

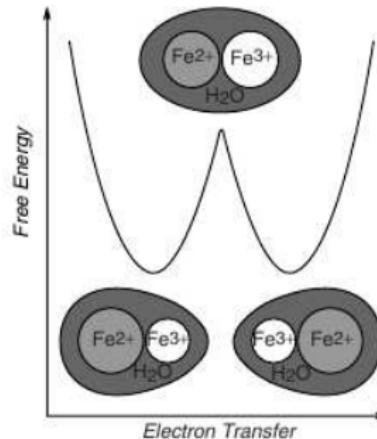
If the electron transfer occurred this way, then total energy of the system suddenly increases

However, if such a transfer occurred in the absence of absorption of light, this mechanism would violate the law of energy conservation

Accordingly, for a thermal electron transfer to proceed, an appropriate redistribution of orientations of solvent molecules in the vicinity of each ion needs to occur prior to ET

With a suitable such fluctuation both the Franck-Condon principle and energy conservation can be satisfied simultaneously, whereas the latter would be violated in the absence of this fluctuation

The need for solvent reorganization

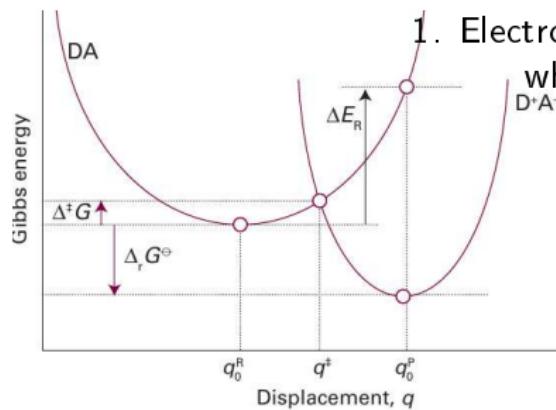


Note the smaller cavity around the triple ion

At the location where free energy for electron transfer is minimal the solvation is symmetric

An environment such as a protein has lower reorganization energy than water and so the rate of electron transfer is higher

Electron transfer theory : diabatic potential curves - adiabatic curves cannot cross;
reaction coordinate : combination of ion-ion separation and solvent reorganisation



1. Electrons transferred by tunnelling through PE barrier,
whose height is partly determined by ionization
energies of DA and D^+A^- complexes

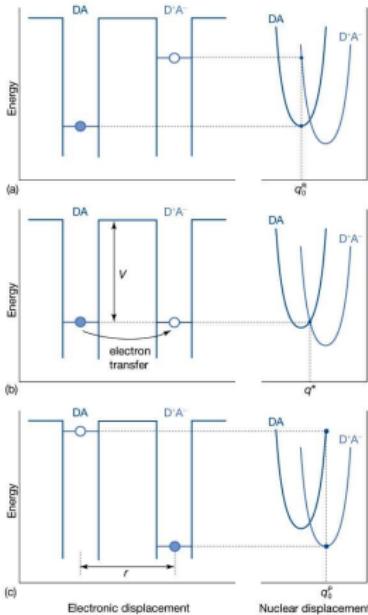
Electron tunnelling influences magnitude of $\kappa\nu$

2. DA and solvent molecules surrounding it
undergo structural rearrangements
prior to electron transfer

Energy associated with these rearrangements and $\Delta_r G^\ominus$ determine $\Delta^\ddagger G$

electronic energy

nuclear motion



- (a) At nuclear configuration q_0^R , electron to be transferred in DA is in HOMO and energy of LUMO of D^+A^- is too high to be good electron acceptor
- (b) As nuclei rearrange to configuration q^* , DA and D^+A^- become degenerate and electron transfer occurs by tunneling through barrier of height V and width r , edge-to-edge distance between donor and acceptor
- (c) system relaxes to equilibrium nuclear configuration of D^+A^- denoted by q_0^P ,

where $E_{\text{LUMO, DA}} > E_{\text{HOMO, } D^+A^-}$

1. Electrons transferred by tunnelling through potential energy barrier, whose height is partly determined by ionization energies of DA and D^+A^- complexes
Electron tunnelling influences magnitude of $\kappa\nu$
2. DA and solvent molecules surrounding it undergo structural rearrangements prior to electron transfer.
Energy associated with these rearrangements and $\Delta_r G^\ominus$, determine $\Delta^\ddagger G$

tunnelling : electron tunnels from an electronic level of D, ψ_D , to an electronic level of A, ψ_A

For electronic transition $\psi_A \leftarrow \psi_D$; Rate $\propto |\langle \psi_A | \hat{H}_{DA} | \psi_D \rangle|^2$

Weak coupling : $\langle H_{DA} \rangle^2 = \langle H_{DA}^{r=0} \rangle^2 e^{-\beta r}$; $k_{et} = \frac{2 \langle H_{DA} \rangle^2}{h} \sqrt{\frac{\pi^3}{4 \Delta E_R R T}} e^{-\frac{\Delta^\ddagger G}{R T}}$

electro-active species sufficiently far apart :

ψ_A and ψ_D do not overlap extensively

ex. : cytochrome c-cytochrome b, complex, in which electroactive haem-bound iron ions shuttle between oxidation states +2 and +3

and are ≈ 1.7 nm apart

strongly coupled systems -ex.: mixed-valence, binuclear d-metal complexes : general structure $L_m M^{n+} - B - M^{p+} L_m$ in which electroactive metal ions are separated by bridging ligand B; $r < 1.0$ nm

weak coupling limit applies to large number of electron transfer reactions, including those between proteins during metabolism

The term, $\sqrt{\frac{\pi^3}{4\lambda RT}} e^{-\frac{\Delta^\ddagger G}{RT}}$ should be used only at high T.

At low T, thermal fluctuations alone cannot bring the reactants to TS.

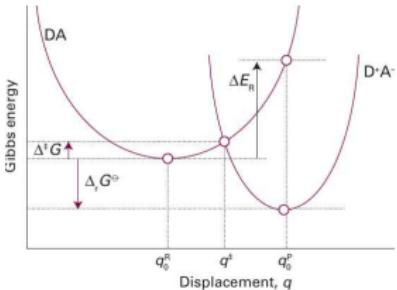
Electron transfer can still occur, by nuclear tunnelling

Full quantum mechanical treatments of electron transfer reactions replace

$\sqrt{\frac{\pi^3}{4\Delta E_R RT}} e^{-\frac{\Delta^\ddagger G}{RT}}$ with Franck-Condon factors, which couple nuclear wavefunctions

and provide a measure of contribution of nuclear tunnelling to rate of electron transfer

Derivation of $\Delta^\ddagger G$: Assume harmonic oscillator free-energy profiles



$$G_{m,R}(q) = \frac{1}{2} N_A \mu \omega^2 (q - q_0^R)^2 + G_{m,R}(q_0^R)$$

$$G_{m,P}(q) = \frac{1}{2} N_A \mu \omega^2 (q - q_0^P)^2 + G_{m,P}(q_0^P)$$

$$\text{At } q = q^*, \quad G_{m,R}(q^*) = G_{m,P}(q^*)$$

write $q^* = q_0^R + \alpha (q_0^P - q_0^R)$: interpolation

$$\begin{aligned} \therefore G_{m,R} \{ q_0^R + \alpha (q_0^P - q_0^R) \} &= \frac{1}{2} N_A \mu \omega^2 \alpha^2 (q_0^P - q_0^R)^2 + G_{m,R}(q_0^R) \\ &= \frac{1}{2} N_A \mu \omega^2 (q^* - q_0^P)^2 + G_{m,P}(q_0^P) \end{aligned}$$

$$\text{or, } \alpha^2 \Delta E_R = \frac{1}{2} N_A \mu \omega^2 (q^* - q_0^P)^2 + \Delta_r G^\Theta - \frac{1}{2} N_A \mu \omega^2 (q_0^R + \alpha (q_0^P - q_0^R) - q_0^P)^2 + \Delta_r G^\Theta$$

$$\text{or, } \alpha^2 \cdot \Delta E_R = (\alpha - 1)^2 \cdot \Delta E_R + \Delta_r G^\Theta \quad \text{or, } \alpha = \frac{1}{2} \left(\frac{\Delta_r G^\Theta}{\Delta E_R} + 1 \right)$$

$$\Delta^\ddagger G = \frac{1}{2} N_A \mu \omega^2 (q^* - q_0^R)^2 = \frac{1}{2} N_A \mu \omega^2 (q_0^R + \alpha (q_0^P - q_0^R) - q_0^R)^2$$

$$= \frac{1}{2} N_A \mu \omega^2 \alpha^2 (q_0^P - q_0^R)^2 = \alpha^2 \Delta E_R = \frac{1}{4} \left(\frac{\Delta_r G^\Theta}{\Delta E_R} + 1 \right)^2 \Delta E_R = \frac{(\Delta_r G^\Theta + \Delta E_R)^2}{4 \Delta E_R}$$

$$\text{if } \Delta_r G^\Theta = -\Delta E_R, \text{ then } \Delta^\ddagger G = 0 \text{ and } \Delta E_R \gg |\Delta_r G^\Theta| \implies \Delta^\ddagger G = \frac{\Delta_r G^\Theta}{2} + \frac{\Delta E_R}{4}$$

It is difficult to measure distance dependence of k_{et} when reactants are ions or molecules free to move in solution.

In such cases, electron transfer occurs after a donor-acceptor complex forms and it is not possible to exert control over r , edge-to-edge distance.

Most meaningful experimental tests of dependence on r are those in which same donor and acceptor are positioned at a variety of distances, perhaps by covalent attachment to molecular linkers

Under these conditions, the term $e^{-\frac{\Delta^\ddagger G}{RT}}$ is a constant

then, $\ln k_{et} = -\beta r + \text{const}$

value of β depends on medium through which electron must travel from donor to acceptor.

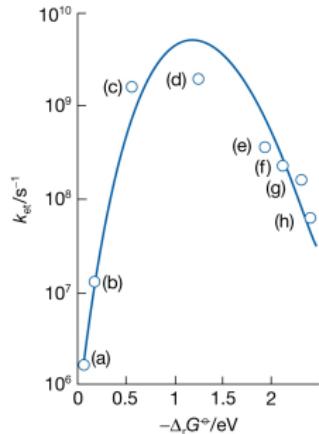
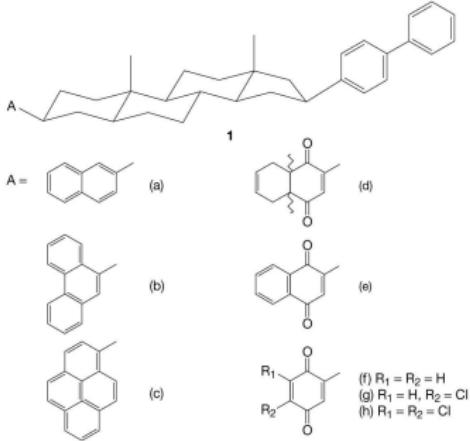
In vacuum, $28 \text{ nm}^{-1} < \beta < 35 \text{ nm}^{-1}$,

whereas $\beta = 9 \text{ nm}^{-1}$ when intervening medium is a molecular link between donor and acceptor.

$$\text{starting from } k_{et} = \frac{2\langle H_{DA} \rangle^2}{h} \sqrt{\frac{\pi^3}{4\Delta E_R RT}} e^{-\frac{\Delta^\ddagger G}{RT}}$$

if r , ΔE_R and $\kappa\nu$ are constant for a series of reactions,

$$\begin{aligned} \ln k_{et} &= \text{const} - \frac{\Delta^\ddagger G}{RT} = -\frac{(\Delta_r G^\ominus + \Delta E_R)^2}{4\Delta E_R RT} + \text{const} \\ &= -\frac{1}{4RT\Delta E_R} (\Delta_r G^\ominus)^2 - \frac{1}{2} \left(\frac{\Delta_r G^\ominus}{RT} \right) + \text{const} \end{aligned}$$



donor: reduced

biphenyl group

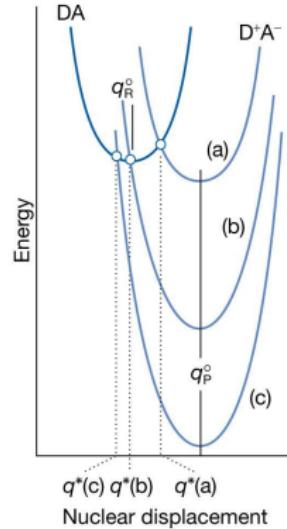
same linker, so r

constant

max at $\Delta_r G^\ominus = -\Delta E_R = 1.2$ eV = 1.2×10^2 kJ mol⁻¹

Explanation for 'inverted region'

- (a) $\Delta^\ddagger G > 0$; TS at $q_a^* > q_0^R$; as process becomes more exergonic, $\Delta^\ddagger G$ decreases and k increases
- (b) When $\Delta^\ddagger G = 0$; TS at $q_b^* = q_0^R$ rate constant for process reaches a maximum as there is no activation barrier to overcome
- (c) As process becomes even more exergonic, $\Delta^\ddagger G$ becomes positive again; now the TS is at $q_c^* < q_0^R$; k decreases steadily as the activation barrier for the process increases with decreasing $\Delta^\ddagger G$



Exergonic electron transfer processes drive synthesis of ATP in mitochondrion during oxidative phosphorylation.

Electron transfer between protein-bound cofactors or between proteins also plays a role in processes such as photosynthesis, nitrogen fixation, reduction of atmospheric N_2 to NH_3 by certain microorganisms, and action of oxidoreductases, enzymes that catalyse redox reactions

Example: cytochrome c and cytochrome c oxidase, which must form an encounter complex before electron transfer can take place
e-transfer between protein-bound cofactors can occur at distances of up to about 2.0 nm, relatively long distance on a molecular scale, with protein providing an intervening medium between donor and acceptor

In Cytochrome c oxidase, intraprotein electron transfer is important.

Bound Cu^{+2} and haem groups work together to reduce O_2 to water in final step of respiration.

controversy on interpretation of protein electron transfer data :

Much of available data may be interpreted with $\beta = 14 \text{ nm}^{-1}$, a value insensitive to primary and secondary structures of protein but depending slightly on density of atoms in the section of protein that separates donor from acceptor

detailed work on specific effect of secondary structure suggests that

$12.5 < \beta < 16 \text{ nm}^{-1}$ when intervening medium consists primarily of α helices and $9 < \beta < 11.5 \text{ nm}^{-1}$ when medium is primarily β sheet.

another view : electron takes specific paths through covalent bonds and H-bonds in protein for optimizing the rate of electron transfer

a different approach :

$$k = Z e^{-\frac{\Delta^\ddagger G}{RT}}$$

if $\Delta E_R \gg |\Delta_r G^\ominus|$, define: Marcus cross-relation: $k_{\text{obs}} = \sqrt{k_{DD} k_{AA} K}$

k_{DD} and k_{AA} are experimental rate constants for electron self-exchange



$$\therefore \Delta^\ddagger G = \frac{\Delta_r G^\ominus}{2} + \frac{\Delta E_R}{4} \implies \Delta^\ddagger G_{DD} = \frac{\Delta E_{R,DD}}{4} \text{ and } \Delta^\ddagger G_{AA} = \frac{\Delta E_{R,AA}}{4}$$

$$\text{or, } k_{DD} = Z_{DD} e^{-\frac{\Delta E_{R,DD}}{4RT}} \text{ and } k_{AA} = Z_{AA} e^{-\frac{\Delta E_{R,AA}}{4RT}}$$

$$\text{assume: } \Delta E_R = \frac{\Delta E_{R,DD} + \Delta E_{R,AA}}{2}$$

$$\therefore \Delta^\ddagger G = \frac{\Delta_r G^\ominus}{2} + \frac{\Delta E_{R,DD} + \Delta E_{R,AA}}{8} \text{ and } k_{\text{et}} = Z e^{-\frac{\Delta_r G^\ominus}{2RT}} e^{-\frac{\Delta E_{R,DD}}{8RT}} e^{-\frac{\Delta E_{R,AA}}{8RT}}$$

$$\text{using } K = e^{-\frac{\Delta_r G^\ominus}{RT}}, \quad k_{\text{obs}} = \sqrt{k_{DD} k_{AA} K} f \text{ where } f = \frac{Z}{\sqrt{Z_{AA} Z_{DD}}} \approx 1$$

kinetic and thermodynamic data for cytochrome c and cytochrome c_{551} two proteins in which haem-bound Fe^{2+} ions shuttle between the oxidation states $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$:

	$k_{ii}/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	E^\ominus/V	
cytochrome c	1.5×10^2	0.260	
cytochrome c_{551}	4.6×10^7	0.286	$k_{obs} = ?$

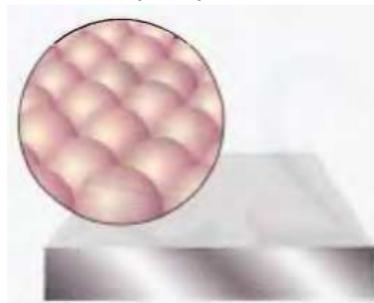


$$E^\ominus = 0.260 - 0.286 = -0.026 \text{ V}$$

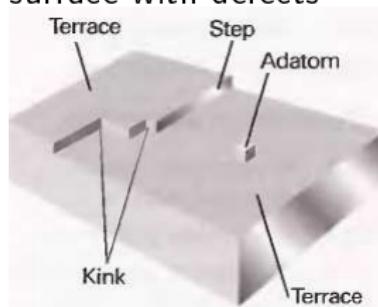
$$\Rightarrow \ln K = -\frac{0.026}{0.02569} \Rightarrow K = 0.36$$

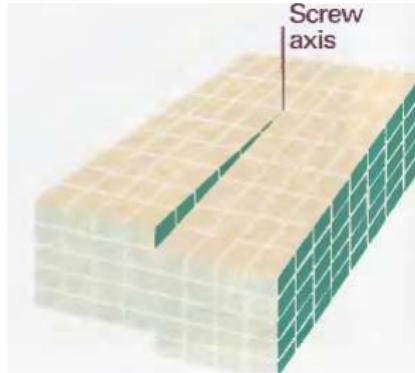
$$k_{obs} = \sqrt{(1.5 \times 10^2)(4.6 \times 10^7)0.36} = 5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

simple picture of a perfect crystal surface (flat)



surface with defects





screw dislocation occurs where one region is pushed up through one or more unit cells relative to another region

The cut extends to the screw axis. As atoms lie along the step the dislocation rotates round the screw axis and is not annihilated

Adsorption : attachment of particles to a solid surface

desorption is the reverse process

adsorbate : substance that adsorbs

material to which it adsorbs : adsorbent or substrate

Under normal conditions

a surface exposed to a gas is constantly bombarded with molecules
and a freshly prepared surface is covered very quickly

$$\text{collision flux : } Z_W = \frac{p}{\sqrt{2\pi m k_B T}}$$

derivation : Consider surface area A perpendicular to the z -axis
 a molecule with $v_z > 0$ will strike the surface within an interval Δt if it lies
 within a distance $v_z \Delta t$ of the surface

\therefore all molecules in vol. $A v_z \Delta t$, with $v_z > 0$, will strike the surface in time Δt
 total number of collisions in this interval is therefore

volume $A v_z \Delta t \times$ number density, \mathcal{N} , of molecules

account for the range of velocities in the sample
 sum the result over all $v_z > 0$ weighted by probability distribution of velocities

$$f(v_z) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{mv_z^2}{2k_B T}}$$

$$\text{no. of collisions} : N = \mathcal{N} A \Delta t \int_0^{\infty} v_z f(v_z) dv_z$$

$$\text{collision flux} : \frac{N}{A \Delta t} = \mathcal{N} \int_0^{\infty} v_z f(v_z) dv_z = \mathcal{N} \sqrt{\frac{k_B T}{2\pi m}} = \frac{p}{k_B T} \sqrt{\frac{k_B T}{2\pi m}} = \frac{p}{\sqrt{2\pi m k_B T}}$$

$$Z_W = \frac{p}{\sqrt{2\pi m k_B T}} = \sqrt{\frac{\frac{N_A}{2\pi k_B}}{MT}} \cdot p = \frac{Z_0 \cdot p}{\sqrt{MT}}; \quad Z_0 = 2.63 \times 10^{24} \text{ m}^{-2} \text{s}^{-1}$$

air : $M = 29$

at $p = 1 \text{ atm}$ and $T = 298 \text{ K}$, $Z_W = 2.9 \times 10^{27} \text{ m}^{-2} \text{s}^{-1}$

1 m^2 of metal surface has $\approx 10^{19}$ atoms

\therefore each atom is struck about 10^8 times each second

Even if only a few collisions leave a molecule adsorbed to the surface, the time for which a freshly prepared surface remains clean is very short

Chemical reactions at a gas-surface interface involve the following sequence of steps :

- ▶ Transport of gas-phase reactants to surface
- ▶ Adsorption of reactants on surface
- ▶ Diffusion of reactants on surface
- ▶ Reaction on surface
- ▶ Desorption of products
- ▶ Transport of products away from surface

Any one or combination of these may be slow and hence

rate-determining

Physisorption and chemisorption

Physisorption :

- long range, weak van der Waals interaction between adsorbate and substrate
- energy released on physisorption : \mathcal{O} (enthalpy of condensation)
- Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion, and a molecule bouncing across the surface will gradually lose energy and finally adsorb to it in the process called **accommodation**

$\Delta H_{\text{physisorption}}$: measured by monitoring rise in temperature of sample of known heat capacity

insufficient to lead to bond breaking, so a physisorbed molecule retains its identity, although it is distorted on surface

Adsorbate	$\Delta_{\text{ad}} H^{\ominus}$ (kJ/mol)
CH ₄	-21
H ₂	-84
H ₂ O	-59
N ₂	-21

data at 298K

Chemisorption : molecules/atoms stick to surface by forming a chemical bond, and find sites that maximize their coordination number with the substrate

$$\Delta H_{\text{chemisorption}} \gg \Delta H_{\text{physisorption}}$$

distance between surface and closest adsorbate atom typically shorter for chemisorption than for physisorption

$\Delta_{ad} H^\ominus$ (kJ/mol) data at 298K

Adsorbate	Adsorbent		
	Cr	Fe	Ni
C ₂ H ₄	-427	-285	-243
CO	..	-192	..
H ₂	-188	-134	..
NH ₃	..	-188	-155

chemisorbed molecule may be torn apart due to unsatisfied valencies of surface atoms

existence of molecular fragments on surface as a result of chemisorption is one reason why solid surfaces catalyse reactions

$$\Delta_{ad} G < 0; \quad \Delta_{ad} S < 0; \quad \Delta_{ad} H < 0$$

Except in special cases, chemisorption must be exothermic

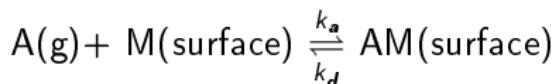
- Exceptions may occur if the adsorbate dissociates and has high translational mobility
 - Ex.: H_2 adsorbs endothermically on glass because there is a large increase of translational entropy accompanying dissociation into atoms that move quite freely over the surface
- $\Delta_{\text{ad}} S_{\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{glass})}$ sufficiently positive to overcome small positive $\Delta_{\text{ad}} H$
- $\Delta_{\text{ad}} H$ depends on extent of surface coverage, mainly because adsorbate particles interact with each other
 - If particles repel each other (as for CO on Pd) adsorption becomes less exothermic ($\Delta_{\text{ad}} H$ less negative) as coverage increases
 - such species settle on surface in a disordered way until packing requirements demand order
 - If adsorbate particles attract one another (as for O_2 on W), then they cluster together in islands, and growth occurs at borders
 - These adsorbates also show order-disorder transitions when they are heated enough for thermal motion to overcome the particle-particle interactions, but not so much that they are desorbed

Adsorption isotherms

Define: fractional coverage, $\theta = \frac{\text{number of adsorption site occupied}}{\text{number of adsorption sites available}}$

Langmuir isotherm :

- Adsorption cannot proceed beyond monolayer coverage
- All sites equivalent
- ability of a molecule to adsorb at a given site independent of occupation of neighbouring sites (no interactions between adsorbed molecules)



$$\left(\frac{d\theta}{dt}\right)_{ad} = k_a p N(1 - \theta) \text{ and } \left(\frac{d\theta}{dt}\right)_{des} = -k_d N\theta$$

At equilibrium: $\left(\frac{d\theta}{dt}\right)_{ad} = \left(\frac{d\theta}{dt}\right)_{des}$, or, $k_a p N(1 - \theta) = k_d N\theta$

$$\text{or, } \frac{\theta}{1 - \theta} = \alpha p, \text{ where } \alpha = \frac{k_a}{k_d} \text{ (dimensions : 1/pressure)}$$

$$\implies \boxed{\theta = \frac{\alpha p}{1 + \alpha p}}$$

Ex. : adsorption of CO on charcoal at 273 K

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
V/cm ³	10.2	18.6	25.5	31.5	36.9	41.6	46.1

(V corrected to 1.00 atm and 273 K)

$$\theta = \frac{\alpha p}{1+\alpha p} \text{ or, } \alpha p = \alpha p\theta + \theta$$

write: $\theta = \frac{V}{V_\infty}$ and divide both sides by $\alpha V \implies \frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{\alpha V_\infty}$

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
$\frac{p}{V}$	1.30	1.44	1.57	1.69	1.81	1.92	2.02

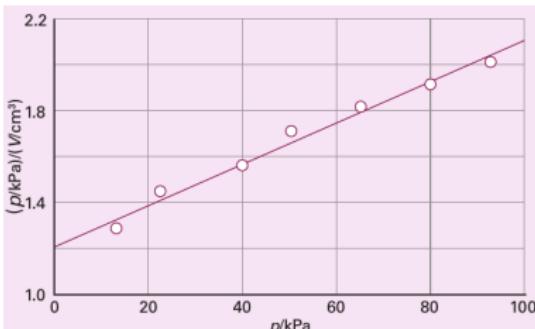
slope=0.009 gives $V_\infty = 111\text{cm}^3$

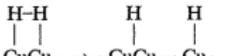
(complete monolayer coverage)

intercept= 1.20

$$\text{gives } \alpha = \frac{1}{111 \times 1.20} = 7.51 \times 10^{-3}\text{kPa}^{-1}$$

volumes in definition of θ are those of the free gas measured under same conditions of temperature and pressure, not the volume the adsorbed gas occupies when attached to surface



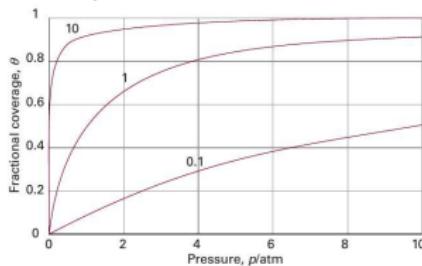


adsorption with dissociation: A_2 adsorbs as 2A , e.g., $\text{H}_2(\text{g}) + \dots \text{Cu} \text{Cu} \dots \rightarrow \dots \text{Cu} \text{Cu} \dots \rightarrow \dots \text{Cu} \text{Cu} \dots \text{Cu} \dots$

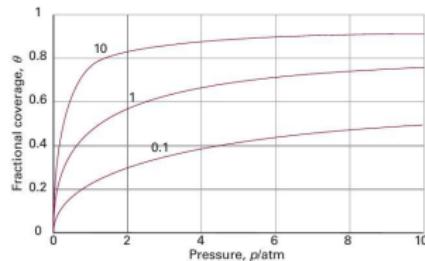
$$\left(\frac{d\theta}{dt}\right)_{ad} = k_a p [N(1 - \theta)]^2 \text{ and } \left(\frac{d\theta}{dt}\right)_{des} = -k_d (N\theta)^2$$

$$\text{Equilibrium: } \theta = \frac{\sqrt{\alpha p}}{1 + \sqrt{\alpha p}},$$

surface coverage depends more weakly on pressure than for non-dissociative adsorption



dissociative



non-dissociative

Experimental procedures must begin with a clean surface
reduce the pressure and reduce the number of impacts on the surface

When $p \sim 0.1\text{mPa}$ (simple vacuum)
collision flux $\sim 10^{18}\text{m}^{-2}\text{s}^{-1}$ \approx one hit per surface atom in each 0.1 s

ultrahigh vacuum (UHV) :

$p \sim 0.1\mu\text{Pa}$ ($Z_W = 10^{15}\text{m}^{-2}\text{s}^{-1}$)

$p \sim 0.1\text{nPa}$ ($Z_W = 10^{13}\text{m}^{-2}\text{s}^{-1}$)

\Rightarrow each surface atom hit once every $10^5 - 10^6$ s or \sim once a day

Microscopy

- ▶ Illuminating a small area of a sample and collecting light with a microscope has been used for many years to image small specimens
- ▶ However, resolution of a microscope, the minimum distance between two objects that leads to two distinct images $\sim \mathcal{O}$ (wavelength of light used)
- ▶ \therefore conventional microscopes employing visible light have resolutions in μm range and are blind to features on a scale of nm

- ▶ **electron microscopy** used to image nm
- ▶ Beam of electrons with a well-defined de Broglie wavelength replaces the lamp in traditional light microscopes
- ▶ Instead of glass or quartz lenses, magnetic fields are used to focus the beam

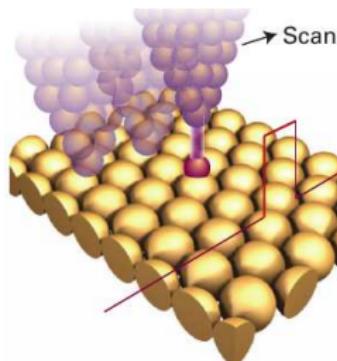
Transmission electron microscopy (TEM)

- ▶ Electron beam passes through the specimen and image collected on a screen
- ▶ Scanning electron microscopy (SEM) electrons scattered back from a small irradiated area of the sample are detected and the electrical signal sent to a video screen
- ▶ An image of the surface is then obtained by scanning the electron beam across the sample
- ▶ electrons focused by magnetic fields—govern the resolution
- ▶ It is now possible to achieve atomic resolution with TEM
- ▶ Resolution on the order of a few nm is possible with SEM

Scanning probe microscopy (SPM)

collection of techniques that can be used to make visible and manipulate objects as small as atoms on surfaces

Scanning tunnelling microscopy (STM)



a platinum–rhodium or tungsten needle is scanned across the surface of a conducting solid. When tip of the needle is brought very close to the surface, electrons tunnel across the intervening space

In 'constant-current mode' of operation, the stylus moves up and down according to the form of the surface

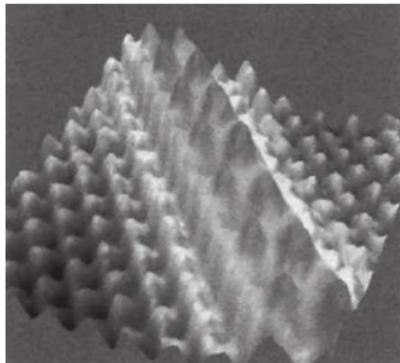
and topography of the surface, including adsorbates, can be mapped on an atomic scale

vertical motion of the stylus is achieved by fixing it to a piezoelectric cylinder, which contracts or expands according to the potential difference it experiences

'constant-z mode'

vertical position of stylus is held constant and current monitored

∴ tunnelling probability is very sensitive to size of the gap, microscope can detect tiny, atom-scale variations in the height of the surface



STM image of Cs doped GaAs

Each 'bump' on the surface corresponds to an atom

In a variation of STM, the tip is used to nudge single atoms around on the surface

making possible fabrication of complex and nm-sized materials and devices

Diffusion characteristics of an adsorbate can be examined by using STM to follow the change in surface characteristics

adsorbed atom makes a random walk across the surface

if d = distance travelled in time τ ,

using 2-D random walk, $d = \sqrt{D\tau}$, where D = diffusion coefficient

value of D for different crystal planes at different temperatures can be determined directly

and $D = D_0 e^{-\frac{E_{a,diff}}{RT}}$, where $E_{a,diff}$ = activation energy for diffusion

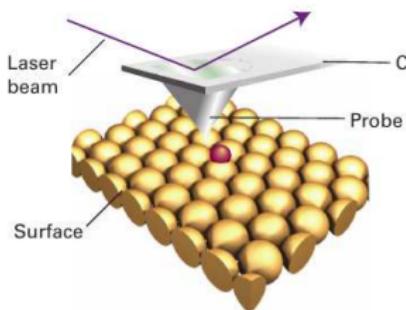
and D_0 = diffusion coefficient for $T \rightarrow \infty$

Diffusion coefficients

Typical values for W atoms on tungsten : $E_{a,\text{diff}} = 57\text{--}87 \text{ kJ mol}^{-1}$
and $D_0 \approx 3.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$

At 800 K, D varies from 7.2×10^{-15} to $7.9 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$

Atomic force microscopy (AFM)



sharpened tip attached to a cantilever is scanned across surface
force exerted by the surface and any molecules attached to it pushes or pulls on the tip and deflects the cantilever
deflection monitored by using a laser beam
∴ no current needs to pass between sample and probe, the technique can be applied to non-conducting surfaces and to liquid samples

'contact mode', or 'constant-force mode' : force between the tip and surface is held constant and the tip makes contact with the surface

This mode of operation can damage fragile samples on the surface

In 'non-contact', or 'tapping mode', the tip bounces up and down with specified frequency and never quite touches the surface

Amplitude of the tip's oscillation changes when it passes over species adsorbed on surface

other techniques to study surface structure :

Ionization techniques

Diffraction techniques

Determination of the extent and rates of adsorption and desorption

monitor rates of flow of gas into and out of the system:
the difference is the rate of gas uptake by the sample

Integration of this rate then gives the fractional coverage at any stage

Gravimetry : sample is weighed on a microbalance during the experiment
The technique commonly uses a quartz crystal microbalance

- Second harmonic generation (SHG):

conversion of an intense, pulsed laser beam to radiation with twice its initial frequency

e.g., adsorption of gas molecules on a surface alters intensity of SHG signal allowing for determination of rates of surface processes and fractional coverage

using pulsed lasers as excitation sources, time-resolved measurements of dynamics of surface processes are possible on timescales as short as fs

- Surface plasmon resonance (SPR) : a sensitive technique

absorption of energy from an incident beam of electromagnetic radiation by surface 'plasmons'

Mobile delocalized valence electrons of metals form a plasma, a dense gas of charged particles

Bombardment of this plasma by light or an electron beam can cause transient changes in distribution of electrons

with some regions becoming slightly denser than others

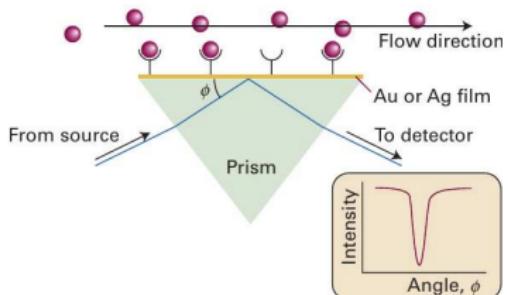
Coulomb repulsion in the regions of high density causes electrons to move away from each other, so lowering their density

Resulting oscillations in electron density, the plasmons, can be excited both in the bulk and on the surface of a metal

A surface plasmon propagates away from the surface
but amplitude of the wave - evanescent wave, decreases sharply with distance from the surface

resonance : absorption that can be observed with appropriate choice of wavelength and angle of incidence of excitation beam

Beam passes through a prism that strikes one side of a thin film of gold or silver



\therefore evanescent wave interacts with material a short distance away from the surface

the angle at which resonant absorption occurs depends on the refractive index of the medium on the opposite side of the metallic film

Changing identity and quantity of material on the surface changes resonance angle

use monochromatic beam and vary the angle of incidence φ

LEED : Low Energy Electron Diffraction

similar to X-ray diffraction

but uses wave character of electrons, and the sample is surface of a solid

The use of low energy electrons (10–200 eV) (wavelengths 100–400 pm) ensures that the diffraction is caused only by atoms on and close to the surface

surface of a crystal rarely has exactly the same form as a slice through the bulk because surface and bulk atoms experience different forces

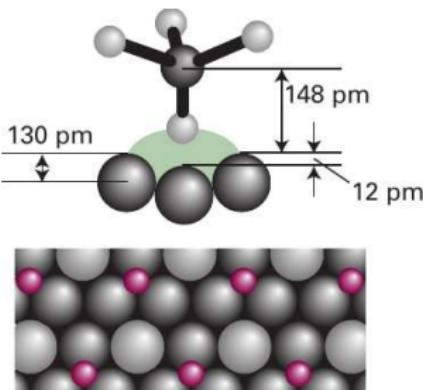
Reconstruction : processes by which atoms on the surface achieve their equilibrium structures

Generally, metal surfaces are simply truncations of the bulk lattice but the distance between the top layer of atoms and the one below is contracted by around 5%

Semiconductors generally have surfaces reconstructed to a depth of several layers

Reconstruction occurs in ionic solids

e.g., in LiF, the Li^+ and F^- ions close to surface lie on slightly different planes



structure of a surface close to the point of attachment of CH_3C^- to the (110) surface of rhodium at 300 K

and changes in positions of metal atoms that accompany chemisorption

Isosteric (fixed coverage) enthalpy of adsorption

dimensionless equilibrium constant: $K = \frac{k_a p^\ominus}{k_d} = \alpha p^\ominus$

$$\Delta_{ad} G^\ominus = -RT \ln(\alpha p^\ominus) \quad \text{and} \quad \left[\frac{\partial \ln(\alpha p^\ominus)}{\partial T} \right]_\theta = \frac{\Delta_{ad} H^\ominus}{RT^2}$$

Ex. 10 cm³ adsorption of CO on charcoal at different temperatures

T/K 200 210 220 230 240 250

p/kPa 4.00 4.95 6.03 7.20 8.47 9.85

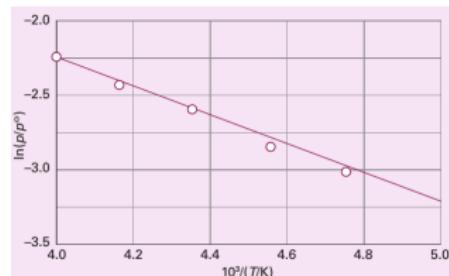
$$\ln \left[(\alpha p^\ominus) \frac{p}{p^\ominus} \right] = \ln(\alpha p^\ominus) + \ln \frac{p}{p^\ominus} \text{ and } (\alpha p^\ominus) \frac{p}{p^\ominus} = \alpha p = \frac{\theta}{1-\theta} = \text{constant}$$

$$\therefore \left[\frac{\partial \ln \frac{p}{p^\ominus}}{\partial T} \right]_\theta = - \left[\frac{\partial \ln(\alpha p^\ominus)}{\partial T} \right]_\theta = - \frac{\Delta_{ad} H^\ominus}{RT^2}$$

$$\text{or, } \left[\frac{\partial \ln \frac{p}{p^\ominus}}{\partial \left(\frac{1}{T} \right)} \right]_\theta = \frac{\Delta_{ad} H^\ominus}{R}$$

$10^3/(T/K)$	5	4.762	4.545	4.348	4.167	4
$-\ln \frac{p}{p^\ominus}$	3.22	3.01	2.81	2.63	2.47	2.32

$$\text{slope} = -0.904, \Delta_{ad} H^\ominus = - (0.904 \times 10^3 \text{ K}) \times R = -7.52 \text{ kJ mol}^{-1}$$



Deviations from Langmuir isotherm :

failure of assumptions - independence and equivalence of the adsorption sites

- enthalpy of adsorption often becomes less negative as θ increases : energetically most favourable sites are occupied first.
- substrate–substrate interactions on the surface can be important
- number of isotherms deal with cases where deviations from Langmuir isotherm are important

BET isotherm: accounts for multilayer adsorption

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \text{ with } z = \frac{p}{p^*}; c = e^{(\Delta_{\text{des}} H^\ominus - \Delta_{\text{vap}} H^\ominus)}$$

p^* =vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles pure bulk liquid

V_{mon} =volume corresponding to monolayer coverage

BET isotherm fits experimental observations moderately well over restricted pressure ranges,

but errs by underestimating extent of adsorption at low pressures and by overestimating it at high pressures.

Temkin isotherm: accounts for varying $\Delta_{\text{ad}} H^\ominus$ with θ

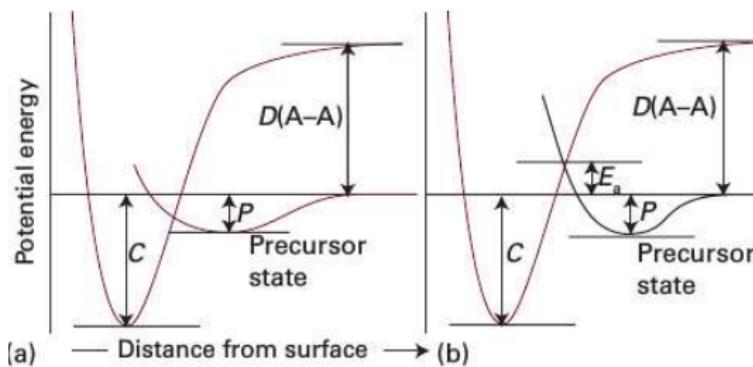
$$\theta = c_1 \ln(c_2 p)$$

Freundlich isotherm : accounts for substrate–substrate interactions

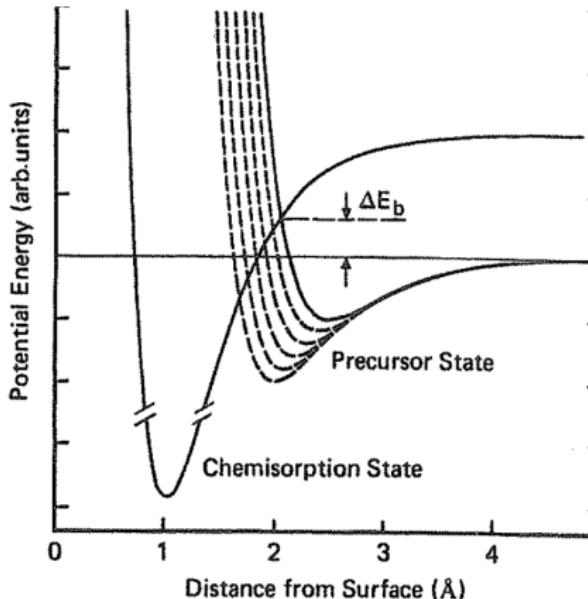
$$\theta = c_1 p^{\frac{1}{c_2}}$$

adsorption and desorption are activated processes, with an activation energy

Precursor state: Before chemisorbing, a molecule becomes trapped temporarily in a weakly bound state
arising from long-range physisorption interactions
⇒ overall intermediate barrier, ΔE_a



Ex. for (b): H₂ on Cu,
 $E_{act} \sim 20-40 \text{ kJ mol}^{-1}$



multiple precursors
for dissociative chemisorption

different curves \implies different
gas-surface systems or different
adsorption sites

for same system

only one curve for chemisorption :
short-range, strongly bound

Barrier between precursor and chemisorbed states allows molecule to become
temporarily trapped on surface before chemisorption For molecule to be
adsorbed to the surface, the barrier must be surmounted

Effectiveness of translational and vibrational energy in surmounting the barrier for dissociative chemisorption differs for different reactions

dissociative chemisorption of CO on Ni(111), estimated $E_{\text{act}} \sim 126 \text{ kJ mol}^{-1}$: no dissociative adsorption at translational energy 190 kJ mol^{-1}

\implies CO must be vibrationally excited for chemisorption

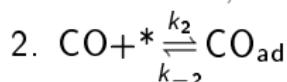
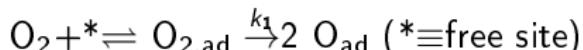
rates are not good criteria for distinguishing between physi- and chemisorption

Chemisorption can be fast if $E_{\text{act}} \approx 0$ and slow if $E_{\text{act}} \gg 0$

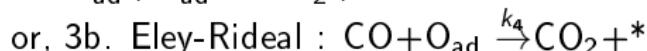
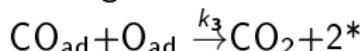
Physisorption is usually fast, but can appear slow if medium is porous

catalytic oxidation of CO to CO_2 :

1. dissociative chemisorption via precursor



- 3a. Langmuir-Hinshelwood :

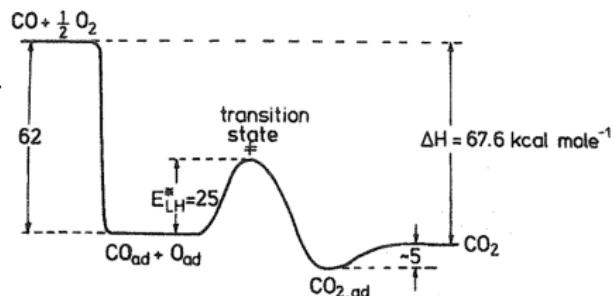


Experiments with Pd, Pt, Ir and Rh surfaces

show dominance of Langmuir-Hinshelwood mechanism

Catalytic formation of CO_2 is slightly influenced by surface structure

Step sites enhance O_2 dissociative chemisorption, but decrease probability of CO_2 formation



All rate constants depend on temperature and surface coverage

Ammonia synthesis on Fe catalyst : $N_2 + 3H_2 \rightarrow 2NH_3$ (Haber) illustrates the role of promoters

rate of NH_3 formation determined by the rate of N_2 dissociative chemisorption on iron surface

Introducing K as adatom promotes the reaction by decreasing the barrier for dissociative adsorption of N_2

Ex. : adsorption experiments for H_2 on different faces of Cu crystal

Face	$E_{act}(\text{kJ mol}^{-1})$
I	28
II	33

ratio of rates of chemisorption on equal areas of the two faces at 250 K is

$$\frac{\text{Rate}(1)}{\text{Rate}(2)} = \frac{Ae^{-\frac{E_{act}(1)}{RT}}}{Ae^{-\frac{E_{act}(2)}{RT}}} = 11$$

Rate of adsorption

sticking probability, $s = \frac{\text{rate of adsorption of particles by the surface}}{\text{rate of collision of particles with the surface}}$

denominator $Z_W = \frac{p}{\sqrt{2\pi m k_B T}}$;

numerator can be measured by observing the rate of change of pressure

values of s vary widely,

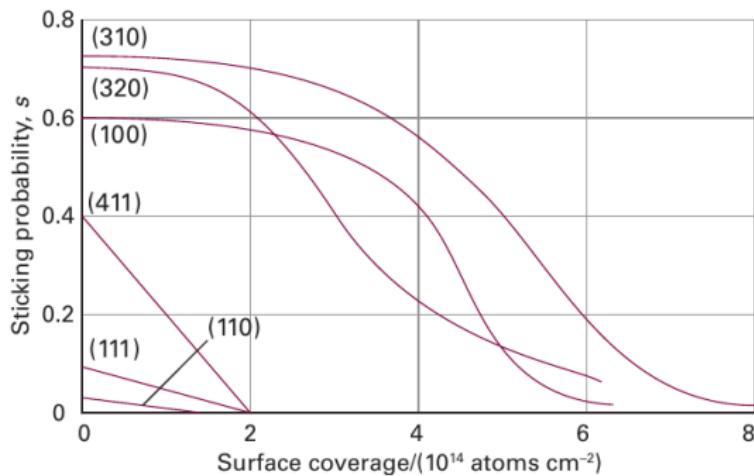
e.g., at room temperature CO has $s \sim 0.1 - 1.0$ for several d-metal surfaces,

but for N_2 on Rhenium, $s < 10^{-2}$

Simple assumption : $s = (1 - \theta) s_0$,

where s_0 = sticking probability on a perfectly clean surface

sticking probability of N_2 on various faces of W crystal and its dependence on surface coverage



Note low sticking probability for the (110) and (111) faces

$s \approx s_0$ until coverage has risen to about 6×10^{13} molecules cm^{-2} and then falls steeply

explanation : probably colliding molecule does not enter the chemisorbed state at once but moves over surface until it encounters an empty site

Rate of desorption: Desorption is always activated because particles have to be lifted from the foot of a potential well physisorbed particle vibrates in its shallow potential well, and might shake itself off the surface after a short time The temperature dependence of first-order rate of departure is expected to be Arrhenius-like, with an activation energy for desorption, $E_d \approx$ enthalpy of physisorption $k_d = A e^{-\frac{E_d}{RT}}$; half-life for remaining on surface depends on T

$$t_{\frac{1}{2}} = \frac{\ln 2}{k_d} = \tau_0 e^{\frac{E_d}{RT}}; \tau_0 = \frac{\ln 2}{A}$$

If $\frac{1}{\tau_0} \approx$ vibrational frequency of weak particle-surface bond ($\approx 10^{12} \text{ Hz}$) and $E_d \approx 25 \text{ kJ mol}^{-1}$, then residence half-lives $\approx 10 \text{ ns}$ at room temp. Lifetimes close to 1 s are obtained by lowering T to $\approx 100 \text{ K}$ For chemisorption, with $E_d \approx 100 \text{ kJ mol}^{-1}$, and $\tau_0 = 10^{-14} \text{ s}$, we get residence half-lives $\approx 3000 \text{ s}$ at room temp and 1 s at 350 K