REACTION DYNAMICS NOTES

Bimolecular Reaction Dynamics

$$k(T) = Ae^{-E_a/RT}$$ factors governing these.

And when equation breaks down

Simple Collision Theory (SCT)

Reactions occur by collisions. Collision energy E_t must exceed the barrier height E_o.
Reaction Rate: collision rate x fraction of collisions with $E_t > E_o$.

Reaction Rate = $\dfrac{-d[A]}{dt} = k(T)[A][B]$

Collision Rate = $Z_{AB}^o[A][B]$

Z_{AB}^o, collision number, = $c_{rel}\,\sigma_c$, $c_{rel} = \left(\dfrac{8kT}{\pi\mu}\right)^{1/2}$ and $\sigma_c = \pi\,d^2$ (collision cross section).

Thermal Rate Coefficient:

$$k_{SCT}(T) = c_{rel}\sigma_c e^{-E_o/RT}$$

When comparing against experiment, reset σ, as $\sigma_x = P\sigma_c$, where P is the probability of reaction on collision, or the **steric factor**.

Collisions between two Atoms and Potential Energy Curves

Separate electronic and nuclear motions of atoms A and B, then solve the Schrodinger Equation for electronic motion:

$$H_e\psi_e = V(R)\psi_e$$

V(R) = dependence of electronic energy on A-B separation, R.

$$H\psi(R) = E\psi(R), \quad E = h\nu(v+\tfrac{1}{2}) + \ldots$$

Force acting on particles at separation R:

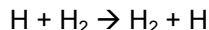$$F(R) = -dV(R)/dR$$

Newton's Laws to calculate motion.
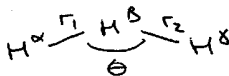Also, glancing collisions –

$$|\,l\,| = \mu\,c_{rel}\,b$$

l is the orbital angular momentum of collision, and b is the impact parameter (distance of closest approach of the atoms in the absence of an interaction potential).

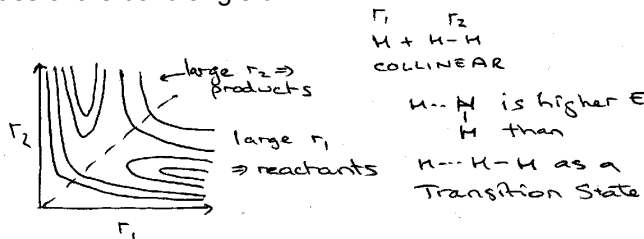### *Collisions between Molecules and Potential Energy Surfaces*

Consider simplest reaction:

$$H + H_2 \rightarrow H_2 + H$$

The PE will depend on 3 coordinates, (r_1, r_2, θ).

Resulting potential energy function (or surface) has the following form plotted as a function of r_1 and r_2 at 2 fixed values of the bond angle θ:

r_1 r_2
H + H–H
COLLINEAR

H··H is higher E than
H··H–H as a Transition State

large r_2 ⇒ products
large r_1 ⇒ reactants

The Potential Energy Surface (PES) provides information on the barrier height to reaction. Vibrational force constants and frequencies can also be determined.

Reaction Coordinate and Reaction Barrier
Reaction Coordinate – minimum PE pathway from reactants to products.
Reaction Barrier, $V^{\ddagger}$ - maximum PE along reaction coordinate. This is often the saddle point on the PES, and can be thought of as a bottleneck through which reactants must pass if they are to proceed to form products.
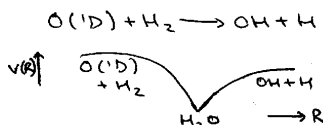
Molecular Collisions
Classical motion over the PES:
Solve classical laws of motion for a set of initial conditions yields classical trajectory. Many needed to obtain accurate k(T). The trajectory can be inelastic (E transfer) or reactive.

Types of PES
Direct reactions with barriers, e.g. $F + H_2 \rightarrow HF + H$.
Reactions with deep PE wells –

Reaction Probability, P(b,γ)
Not all collisions lead to reaction. Depends on angle of approach, γ, and impact parameter, b.

Reaction Cross-Sections
Integral of reaction probability over impact parameter –

$$\sigma_R = \int_{0}^{b,\max} P(b)2\pi b\, db$$

$$\sigma_R = p\,\pi\,b_{max}^{2}$$

P(b) is the opacity function = $N_{reactive}(b) / N_{total}(b)$, where the N(b)'s are trajectories.

Unsurprisingly, head-on collisions tend to be more reactive than glancing-blows.

### Cross-section dependence on Collision Energy
For a reaction with a barrier, collisions at high ε_t are more reactive than those at low ε_t.

Rate constant should therefore be obtained from reaction cross-sections by evaluating the Maxwell-Boltzmann average of $c_{rel}\sigma_R(\varepsilon_o)$:

$$k(T) = \int_{0}^{\infty} c_{rel}\sigma_r(\varepsilon_o)\int \varepsilon_t\, d\varepsilon_t$$

Reaction cross-sections can depend on reactant's vibrational and rotational state. Reaction barrier is a bottleneck so motion of reactants along specific coordinates is required for reaction.

State-Specific Rate Constants

$$A + BC(i) \rightarrow AB + C$$
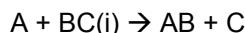
$$k(T) = \sum_{i} P_i k_i(T)$$

Transition State Theory
- Quantum Mechanical calculations only possible for N ≤ 4.
- N ≥ 4 classical trajectory calculations are time consuming.
- Both require full PES.
- SCT doesn't work very well.

Key advantage with TST is only need PES at transition state.

$$A + BC \rightarrow ABC^{\ddagger} \rightarrow AB + C$$

Motion orthogonal to the minimum energy path (MEP) corresponds to conventional (symmetric) stretching and bending vibrations of ABC.
Motion along MEP corresponds to translational motion over barrier.

Reaction Rate Constants and Probability

The rate of reactant approach (the number per unit length per second) at relative velocities between $c \rightarrow c + dc$.

$$d\text{Rate} = n_A n_{BC}\, c\, f(c)\, dc$$

$f(c)$ is the one dimensional Maxwell-Boltzmann distribution of relative velocities.
Reaction Rate is the approach rate times the probability of reaction at a given collision energy, $P(\varepsilon_t)$.

$$d\text{Reaction Rate} = n_A n_{BC} P(\varepsilon_t) c\, f(c)\, dc$$

Hence, thermally average reaction rate is:

$$-\frac{dn_A}{dt} = n_A n_{BC} \int_0^\infty P(\varepsilon_t) c\, f(c)\, dc$$

In terms of kinetic energies:

$$k(T) = \int_0^\infty P(\varepsilon_t) f(\varepsilon_t) \frac{d\varepsilon_t}{\mu}, \; \varepsilon_t = \tfrac{1}{2}\mu c^2$$

$$f(\varepsilon_t) = \frac{\mu}{h q_t} e^{-\varepsilon_t / kT}$$

q_t is a one dimensional translational partition function (per unit length).

$$q_t = \left(\frac{2\pi\mu kT}{h^2}\right)^{1/2}$$

and represents the number of thermally accessible translational states per unit length at temperature T. Substitution into the expression for $k(T)$:

$$k(T) = \frac{1}{h q_t} \int_0^\infty P(\varepsilon_t) e^{-\varepsilon_t / kT} d\varepsilon_t$$

In many dimensions, the above equation applies to each quantum state, weighted by the Boltzmann population for the molecules in these states:

$$k(T) = \frac{1}{h q_t} \int_0^\infty \sum_n P(\varepsilon_t) \frac{g_n e^{-\varepsilon_n / kT}}{q_{A:int}\, q_{BC:int}} e^{-\varepsilon_t / kT} d\varepsilon_t$$

where g_n is the degeneracy of state n and:

$$q_{A:int} = q_{A:el} \text{ and } q_{BC:int} = q_{BC:rot} q_{BC:vib} q_{BC:el}$$

with

$$q_t = \left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} \text{ (now in 3 dimensions)}$$

More compactly written as:

$$k(T) = \frac{1}{h q} \int_0^\infty N(\varepsilon) e^{-\varepsilon / kT} d\varepsilon$$

where $N(\varepsilon) = \sum_n P_n(\varepsilon)$ with $\varepsilon = \varepsilon_t + \varepsilon_n$. $N(\varepsilon)$ is called the Cumulative Reaction Probability, and q is the total reactant partition function.
Equation is exact, providing reactants are in thermal equilibrium.

Transition State

TST approximates $N(\varepsilon)$.

Assumptions:
1. Reactants are in thermal equilibrium.
2. Motion along MEP is separable from that orthogonal to it.
3. Motion along reaction coordinate is classical.
4. Motion along MEP is direct (no re-crossing rule).

From Assumption 2, $\varepsilon = \varepsilon_t^{\ddagger} + \varepsilon_n^{\ddagger} + \varepsilon_o$, where ε_o is the different in zero point energies between reactant and Transition State.

Assumptions 3 and 4 imply:
$P_n(\varepsilon_t^{\ddagger}) = 1$ if $\varepsilon_t^{\ddagger} > 0$.

This gives:

$$k(T) = \frac{\sum_n g_n^{\ddagger} e^{-\varepsilon_n^{\ddagger}/kT}}{h q_t q_{A:int} q_{BC:int}} e^{-\varepsilon_o/kT} \int_0^{\infty} e^{-\varepsilon_t^{\ddagger}/kT} d\varepsilon_t^{\ddagger}$$

$$\Rightarrow k(T) = (\frac{kT}{h}) \left(\frac{q_{int}^{\ddagger}}{q_t q_{A:int} q_{BC:int}} \right) e^{-\varepsilon_o/kT}$$

where,

$$q_{int}^{\ddagger} = q_{rot}^{\ddagger} q_{vib}^{\ddagger} q_{el}^{\ddagger},$$

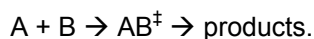$$q_t = \left(\frac{2\pi\mu kT}{h^2} \right)^{3/2}, etc.$$

More simply,

$$k(T) = \frac{kT}{h} \frac{q^{\ddagger}}{q_A q_{BC}} e^{-\varepsilon_o/kT}$$

Units = m^3 molec^{-1} s^{-1}.

Checking Validity wrt SCT:

$$A + B \rightarrow AB^{\ddagger} \rightarrow products.$$

Applications of Transition State Theory

Estimating the Steric Factor –

$$A + B \rightarrow AB$$

$$k_{SCT}(T) \sim \frac{kT}{h} \frac{q_{rot}^2}{q_t^3} e^{-\varepsilon_o/kT}$$

$$AB + CD \rightarrow ABCD^{\ddagger} \rightarrow products$$

Proceeding via a non-linear Transition State:

$$k_{TST}(T) \sim \frac{kT}{h} \frac{q_{rot}^3 q_{vib}^5}{q_t^5 q_{rot}^4 q_{vib}^2} e^{-\varepsilon_o/kT}$$

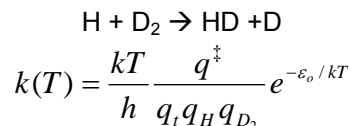Steric Factor,

$$P = k_{TST}(T)/k_{CST}(T) \sim (q_{vib}/q_{rot})^3$$

Hence, $P \sim 10^{-2} - 10^{-4}$.

Generally, P tends to fall with increasing reactant complexity.

Rate Constant Calculation –

$$H + D_2 \rightarrow HD + D$$

$$k(T) = \frac{kT}{h} \frac{q^{\ddagger}}{q_t q_H q_{D_2}} e^{-\varepsilon_o / kT}$$

Transition State is linear. At 300K,

$$\varepsilon_o = V^{\ddagger} + \varepsilon_z^{HDD} - \varepsilon_z^{DD}$$

$$q_t = \left(\frac{2\pi\mu kT}{h^2} \right)^{3/2}$$

For the transition state,

$$I^{\ddagger} = \frac{m_1 m_2 + 4 m_1 m_3 + m_2 m_3}{M} r_e^{\ddagger 2}$$

$$and \ B^{\ddagger} = \frac{h^2}{2I^{\ddagger}}$$

$$q_{rot}^{\ddagger} = kT \Big/ B^{\ddagger}$$

$$q_{vib}^{\ddagger} = \prod_i (1 - e^{h\nu_i / kT})^{-1}$$

For the reactants, I, B, q_{rot} and q_{vib} can be calculated easily using formulae.
For this reaction, subbing values in:

$$k(T) = 8.63 \times 10^{-18} \ cm^3 \ molec^{-1} \ s^{-1}.$$

Experimentally, obtain ~ 21 x 10^{-18}.
Reason for difference is neglect of tunnelling in TST.

Tunnelling Corrections
Motion over barrier not always classical.
Transmission probability for a square potential energy barrier:

$$T = \frac{\psi(b)^2}{\psi(a)^2} \sim e^{-2k(b-a)}$$

$$k = \sqrt{\frac{2\mu(V^{\ddagger} - \varepsilon_r)}{h^2}}$$

valid if k(b-a) >> 1.

Tunnelling is most important for light particles passing through thin barriers, and most apparent at low temperature.

Failings of Transition State Theory
TST assumes classical motion along MEP is direct, i.e. no re-crossing. The importance of this depends on the shapes of the PES, the total energy and the masses of the species involved.
Re-crossing is a minor problem at room temperature for reactions with substantial barriers.
When it is important, TST yields an upper-bound to the classical rate constant.

Temperature Dependence
A + BC reaction via linear Transition State. Assume $q_{vib} \rightarrow 1$, and extract T-dependence of q_{rot} and q_{vib}:

$$k(T) \approx CT \frac{T}{T^{3/2} T} e^{-E_o / RT}$$

$$= CT^{-1/2} e^{-E_o / RT}$$

In general, T-dependence of bimolecular rate constant:

$$k(T) = CT^n e^{-E_o / RT}$$

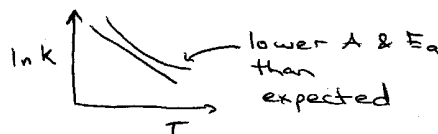From definition of Activation Energy:

$$\frac{d \ln k(T)}{dT} = \frac{nRT + E_o}{RT^2} = \frac{E_a}{RT^2}$$

i.e. $E_a = E_o + nRT$

Often $E_o \gg RT$, and T-dependence is dominated by E_o.
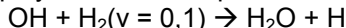
Non-Arrhenius Behaviour

Tunnelling can lead to curvature in Arrhenius plot:

The T-dependence of the partition functions appearing in the A-factor can also cause curvature. Important when $E_o \leq nRT$.
Radical Recombination reactions also $E_o \sim 0$.

Also arises if the rate constant displays a marked dependence on reactant quantum state:

$$OH + H_2(v = 0,1) \rightarrow H_2O + H$$

Vibrational excitation of H_2 to v=1 increases k by factor of over 100 ($k_1(T) \gg k_0(T)$).

$$K(T) = P_o k_o(T) + P_1 k_1(T)$$

With

$$P_v = \frac{e^{-\Delta\varepsilon_v / kT}}{q_{H_2:vib}}$$

Reaction barrier occurs late along reaction coordinate once the H-H bond is stretched (i.e. the PES has a "late barrier").

Curvature for reaction is reasonably well accounted for by TST once tunnelling correction is made.

Kinetic Isotope Effects, KIEs

TST provides a reliable estimate of the kinetic isotope effect:

$$\ln \frac{k_H}{k_D} = \ln \frac{A_H}{A_D} - \frac{E_{a,H} - E_{a,D}}{RT}$$

The last term often dominates.

Upper bound to the KIE may be obtained assuming that ZPEs of Transition State species are insensitive to isotopic substitution:

$$(E_{a,H} - E_{a,D}) \approx E_{o,H} - E_{o,D} \approx E_{z,D} - E_{z,H}$$

The difference in Activation Energies is then approximately the difference in the reactant zero point energies, E_z.

Thermodynamic Formulation of TST

Useful as:
*   TST structure and vibrational frequencies may not have been calculated.
*   For reactions in solution the partition functions are not simply defined (e.g. role of solvent).

Also, may be a simpler expression possible.
TST uses partition functions per unit volume.

$$S = \frac{U - U(0)}{T} + k \ln Q, \text{ and } Q = q^N/N!$$

Hence,

$$S^o = \frac{U^o - U^o(0)}{T} + R \ln \frac{q^o}{N_A} + R$$

Also, H = U + pV = U + NkT, and H(0) = U(0).

$$S^o = \frac{H^o - H^o(0)}{T} + R \ln \frac{q^o}{N_A}$$

$$\frac{q^o}{N_A} = q'\frac{V^o}{N_A} = q'\frac{kT}{p^o}$$

$$\therefore q' = \frac{q^o}{V^o} = \frac{kT}{p^o}e^{S^o/R_e - (H^o - H^o(0))/RT}$$

Use k(T) expression for A + BC reaction and multiply to N_A *units change). Then,
$N_A \varepsilon_o = \Delta^{\ddagger}U^o(0)$ and the above gives:

$$k(T) = \frac{RT}{p^o}\frac{kT}{h}e^{\Delta^{\ddagger}S^o/R_e - \Delta^{\ddagger}H^o/RT}$$

$\Delta^{\ddagger}H^o$ and $\Delta^{\ddagger}S^o$ are the enthalpy and entropy of activation.

Comparison with Arrhenius

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

$$\Rightarrow k(T) = \frac{RT}{p^o}\frac{kT}{h}e^{\Delta^{\ddagger}S^o/R_e - \Delta^{\ddagger}H^o/RT}$$

$$\Rightarrow E_a = \Delta^{\ddagger}H^o + 2RT$$

$$Thus,$$

$$k(T) = e^2\frac{RT}{p^o}\frac{kT}{h}e^{\Delta^{\ddagger}S^o/R_e - \Delta^{\ddagger}H^o/RT}$$

Entropy of Activation

$$\Delta^{\ddagger}S^o = S_{\ddagger}^o - S_A^o - S_{BC}^o$$

Represent change in entropy in going from reactants to Transition State.
For gas phase bimolecular reactions, $\Delta^{\ddagger}S^o < 0$, reflecting the loss of translational entropy on forming single species from 2.

Applications – Thermochemical Kinetics

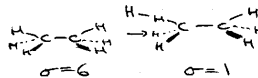$$\Delta^{\ddagger}S^o = S_{\ddagger}^o - S_H^o - S_{C_2H_6}^o$$

Translational Contribution:

$$m_{C_2H_6} \simeq m_{C_2H_7}, \therefore S_{tr,\ddagger}^o \simeq S_{tr,C_2H_6}^o$$

Rotational contribution:

$$I_{C_2H_6} \simeq I_{C_2H_7}$$

Also symmetry numbers:

$$H_3C-C \begin{smallmatrix}H\\H\end{smallmatrix} \rightarrow H_3C-C \begin{smallmatrix}H\\H\end{smallmatrix} \quad \begin{matrix}H-H\end{matrix}$$

$$\sigma = 6 \qquad \sigma = 1$$

$$\Rightarrow \sigma_{C_2H_6} = 6\sigma_{C_2H_7}$$

$$q \propto \sigma e^{S^o}$$

$$\Rightarrow \frac{S_{C_2H_6}}{R} \ln \sigma = \frac{S_{\ddagger}^o}{R} + \ln 6\sigma$$

$$\Rightarrow S_{\ddagger,rot}^o = S_{C_2H_6,rot}^o + R \ln 6.$$

Vibrational contribution:
ignore changes in vibrational & internal rotational partition functions on forming H-H-C.

$$\Rightarrow S_{\ddagger,vib}^o \gtrsim S_{C_2H_6,vib}^o$$

Electronic contribution:
C_2H_6 has singlet ground state (no unpaired e)
$C_2H_7^{\bullet}$ — 1 unpaired electron $\Rightarrow S = 1/2$
$\Rightarrow$ doublet.

$q_{el} \approx g_0$, $g_0 = 2S+1 \Rightarrow$ 1 for C_2H_6
2 for C_2H_7

$\Rightarrow S_{\ddagger,el}^{\ominus} \gtrsim S_{el,C_2H_6}^{\ominus} + R \ln 2$.

Combining these, lower limit:

$$S_{\ddagger}^{\ominus} \gtrsim S_{C_2H_6}^{\ominus} + R \ln 2 + R \ln 6$$

Considering entropy of H-atom:

$$S_H^{\ominus} = k \ln Q_{trs} + kT \left(\frac{\partial \ln Q_{trs}}{\partial T} \right)_V$$

$$\frac{S_H}{R} = \ln \left(M^{3/2} T^{5/2} \left(\frac{\beta}{p^{\ominus}} \right)^{-1} \right) + \underset{-1.165R}{\underline{constant}}$$

$$S_H = R \ln 400^{5/2} \, 1^{3/2} \cdot 1 \; - 1.165R$$
$$= 119 \text{ J K}^{-1} \text{mol}^{-1}.$$

$$\therefore \Delta^{\ddagger} S^{\ominus} = S_{\ddagger}^{\ominus} - S_{C_2H_6}^{\ominus} - S_H^{\ominus}$$
$$= R \ln 6 + R \ln 2 - 119$$
$$\gtrsim -99.34 \text{ J K}^{-1} \text{mol}^{-1}$$

$$A = e^2 \left(\frac{RT}{p^{\ominus}} \right) \left(\frac{kT}{h} \right) e^{\Delta^{\ddagger} S/R}$$

$$= 1.33 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}. \checkmark$$

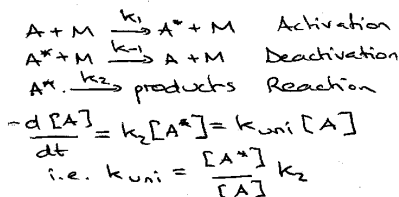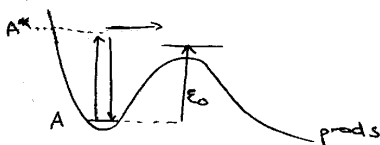$A_{exp} = 1.0 \times 10^{11}$, so ~ 1 order of magnitude out.

Unimolecular Reaction Dynamics

Relevance –
- (i) Thermal Unimolecular Reactions.
- (ii) Radical Recombination.
- (iii) Chemical Activation.
- (iv) Photodissociation.

Thermal Unimolecular Reactions

Lindemann Mechanism:

$A + M \xrightarrow{k_1} A^* + M$ Activation
$A^* + M \xrightarrow{k_{-1}} A + M$ Deactivation
$A^* \xrightarrow{k_2}$ products   Reaction
$-\frac{d[A]}{dt} = k_2[A^*] = k_{uni}[A]$
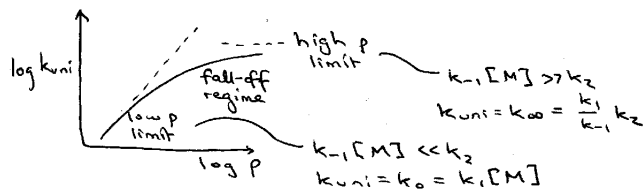i.e. $k_{uni} = \frac{[A^*]}{[A]} k_2$

Steady State:

$$[A^*] = \frac{k_1[M][A]}{k_{-1}[M] + k_2}$$
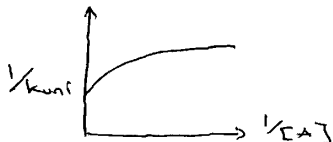
Unimolecular Rate Constant:

$$k_{uni} = \frac{[A^*]}{[A]} k_2 = \left[\frac{[k_1[M]}{k_{-1}[M] + k_2} \right]^{\frac{1}{2}}$$

Fall-off Curve – variation of k_{uni} with pressure:

Limitations:

$[M]_{1/2}$ is the concentration (proportional to pressure) at which $k_{uni} = k_\infty/2$
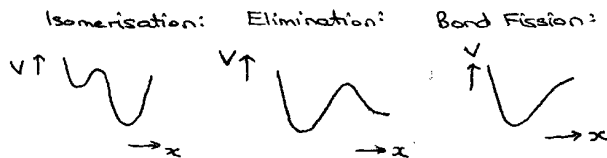
$$[M]_{1/2}^{calc} = k_\infty/k_1$$

Fix k_∞ to experimental value.
SCT to calculate k_1:

$$k_1 = pZ_{AM}^o e^{-\varepsilon_o/kT}$$
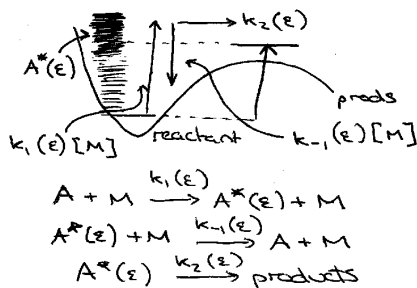
ε_o is the energy threshold to reaction (critical energy).

Unimolecular Reaction Mechanisms

Different MEPs:

Energy Dependent Lindemann Scheme –

$$A + M \xrightarrow{k_1(\varepsilon)} A^*(\varepsilon) + M$$
$$A^*(\varepsilon) + M \xrightarrow{k_{-1}(\varepsilon)} A + M$$
$$A^*(\varepsilon) \xrightarrow{k_2(\varepsilon)} products$$

Steady State –

$$\frac{[A^*(\varepsilon)]}{[A]} = n(\varepsilon) = \frac{k_1(\varepsilon)[M]}{k_{-1}(\varepsilon)[M] + k_2(\varepsilon)}$$

Contribution to k_{uni} at energy ε is $n(\varepsilon)k_2(\varepsilon)$.
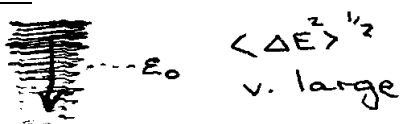
$$k_{uni} = \int_{\varepsilon_o}^{\infty} n(\varepsilon)k_2(\varepsilon)d\varepsilon$$

$n(\varepsilon)d\varepsilon$ is the fraction of A molecules in the energy range $\varepsilon \rightarrow \varepsilon + d\varepsilon$
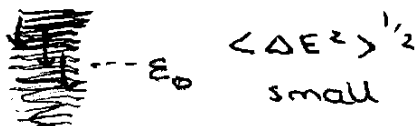
Deactivation – The Strong Collision Assumption

Deactivation tends to be efficient and vary only mildly with energy.

Strong Collisions:

$\langle \Delta E^2 \rangle^{1/2}$
v. large

Assume every collision renders A*(ε) unreactive.

Weak Collisions:

$\langle \Delta E^2 \rangle^{1/2}$
small

Efficiency of deactivation increases with increasing complexity of the molecule.

Problems to Address

High pressure limit there is a rapid pre-equilibrium.

$$A + M \Leftrightarrow A^{0}(\varepsilon) + M$$

$$n(\varepsilon) = \left(\frac{[A*(\varepsilon)]}{[A]} \right) = \frac{k_1(\varepsilon)}{k_{-1}} = \frac{g(\varepsilon)e^{-\varepsilon/kT}}{q_A}$$

$g(\varepsilon)$ is the degeneracy (density of states).
As the pressure drops, equilibrium between A* and A is perturbed by the reaction.
The most highly excited A* molecules are preferentially depleted by reaction (bigger k_2).
If $n(\varepsilon)$ changes with p, k_{uni} is likely to as well.

Energy Dependent Reaction Rates

Radical Recombination:

A + B → AB* k_a [recombination]
AB* → A + B k_{-a} [dissociation]
AB* + M → AB + M k_b [stabilisation]
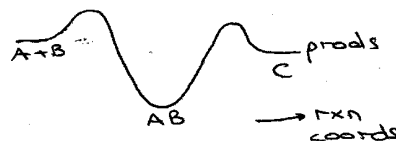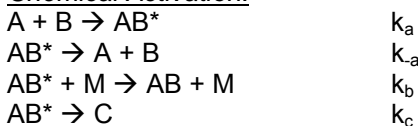
$$-\frac{d[A]}{dt} = k_{rec}[A][B]$$

SSA: AB* → $k_{rec} = \dfrac{k_a k_b [M]}{k_{-a} + k_b [M]}$

i)   Low Pressure: $k_{rec} = \dfrac{k_a k_b}{k_{-a}}[M]$

ii)   High Pressure: $k_{rec} = k_a$

Formal reverse of a bond fission. $K_c = k_{rec}/k_{uni}$

Chemical Activation:

A + B → AB* k_a
AB* → A + B k_{-a}
AB* + M → AB + M k_b
AB* → C k_c

Reaction Rate:
$$\frac{d[C]}{dt} = k_c[AB*]$$
Stabilisation Rate:
$$\frac{d[AB]}{dt} = k_b[M][AB*]$$

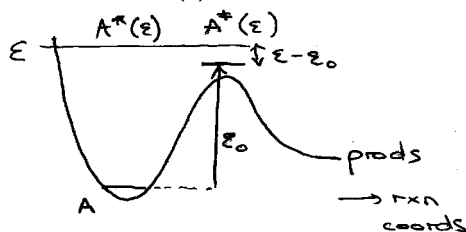$$\frac{reaction\ rate}{stabilisation\ rate} = \frac{[C]}{[AB]} = \frac{k_c}{k_b[M]}$$

Lifetime of AB* = $\dfrac{1}{k_{-a} + k_b[M] + k_c}$

Reaction Rate Constant, $k_I(\varepsilon)$

RRK Theory
For unimolecular reactions.
Distinguish between energised molecule A*(ε) and activated molecule $A_m^{\ddagger}(\varepsilon)$.

Assumptions:
- Ignore A* rotation.
- Molecule A has s identical harmonic oscillators with energy ε.
- $A^{\ddagger}(\varepsilon)$ also has s identical oscillators, but energy ε_o is localised in one vibrational mode, the reaction coordinate.
- $A^{\ddagger}$ falls apart with rate constant $k^{\ddagger}$, independent of energy.
- Vibrational Energy flows freely in energised and activated species.

Reaction Rate Constant:

$$k_2(\varepsilon) = k^{\ddagger}\frac{[A^{\ddagger}(\varepsilon)]}{[A*(\varepsilon)]} = k^{\ddagger}r^{\ddagger}(\varepsilon)$$

RRK Theory is a statistical theory of unimolecular reactions.
If energy flow is rapid and random (free), the vibrational energy in A* will be distributed statistically.

The fraction of A* molecules with energy ε_o localised in one bond (reaction coordinate) is:
$$r^{\ddagger}(\varepsilon) = [(\varepsilon-\varepsilon_o)/\varepsilon]^{s-1}$$

Thus,

$$k_2(\varepsilon) = k^{\ddagger}[(\varepsilon-\varepsilon_o)/\varepsilon]^{s-1} \qquad \varepsilon \geq \varepsilon_o$$

Interpretation –
As ε increases, probability of localising ε_o in reaction coordinate also increases. Thus, $k_2(\varepsilon)$ increases.
Increasing s reduces probability that one specific oscillator (reaction coordinate) receives enough energy, ε_o, for reaction to occur, therefore $k_2(\varepsilon)$ falls.

How Does an Energy Molecule Behave?
Molecules close to dissociation can be observed spectroscopically.
- Direction Absorption Spectroscopy (vibrational overtone).
- Emission Spectroscopy.

IVR and Free Energy Flow
When vibrational energy is low it stays localised in the (nearly harmonic) normal modes.
As vibrational energy increases, motion becomes more chaotic (delocalises). Induced by anharmonicity of the PES.
Assumption of rapid IVR breaks down for small molecules with small reaction barriers, ε_o.

Does RRK Theory Work?
- $k^{\ddagger}$ and the number of oscillators s need to be adjusted to fit experiment.
- s typically takes a value s ~ ½ (3N-6).
- Assumption that all modes are harmonic and have same frequency does not work.
- Rotation can play a role.

Some can be addressed in a more sophisticated statistical theory – RRKM Theory.

Degeneracy in n(ε)

$g(\varepsilon)$ = vibrational density of states in $n(\varepsilon) = \dfrac{k_1(\varepsilon)}{k_{-1}} = \dfrac{g(\varepsilon)e^{-\varepsilon/kT}}{q_A}$

How does degeneracy arise?
3 quanta to distribute in 3 identical harmonic oscillators.
In general,

$$g_i = \frac{i+s-1}{i!(s-1)!} = \frac{5!}{3!2!} = 10$$

RRK Expression for $k_1(\varepsilon)$

$$\frac{k_1(\varepsilon)}{k_{-1}} = \frac{1}{kT}\frac{1}{(s-1)!}\left(\frac{\varepsilon}{kT}\right)^{s-1}e^{-\varepsilon/kT}$$

With strong collision approximation, k_{-1} is the collision number, Z_{AM}°.

$$\varepsilon_{max} = (s-1)k_BT$$

$$\frac{k_1(\varepsilon_{max})}{k_{-1}} = \frac{1}{(s-1)!}(s-1)^{s-1}e^{-(s-1)/kT}$$

Hinshelwood Expression –

$$\frac{k_1}{k_{-1}} = \int_0^{\infty}\frac{k_1(\varepsilon)}{k_{-1}}d\varepsilon \approx \frac{1}{(s-1)!}\left(\frac{\varepsilon_o}{kT}\right)^{s-1}e^{-\varepsilon_o/kT}$$

Steric Factor,

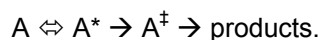$$P = \frac{1}{(s-1)!}\left(\frac{\varepsilon_o}{kT}\right)^{s-1}$$

RRK Expression for k_{∞}
In high pressure limit k_{ni} reduces approximately to:

$$k_{\infty} = \int_{\varepsilon_o}^{\infty}\frac{k_1(\varepsilon)}{k_{-1}}k_2(\varepsilon)d\varepsilon \approx k^{\ddagger}e^{-\varepsilon_o/kT}$$

$k^{\ddagger}$ is the limiting high pressure A factor, A_{∞}.

TST For High Pressure Limit

$$A \Leftrightarrow A^* \rightarrow A^{\ddagger} \rightarrow \text{products.}$$

Because A* is in thermal equilibrium with A at high pressure we can use TST.

$$k_{\infty} = (\frac{kT}{h})(\frac{q^{\ddagger}}{q_A})e^{-\varepsilon_o/kT}$$

In thermodynamic form:

$$k(T) = e\frac{kT}{h}e^{\Delta^{\ddagger}S^o/R_e - E_a/RT}$$

Conclusions
Assumptions that all modes are harmonic and have same frequency render the RRK model of little predictive use.
Statistical idea introduced in RRK Theory (i.e. energy flows freely and rapidly around A*) is an important one, and is still used in modern treatments.
Statistical theories don't work well when reaction rate becomes competitive with rate of free energy flow.