

CHEMICAL REACTION RATES

Trinity Term 2003

Scope of Lectures

A) Bimolecular Reaction Rates

B) Unimolecular Reaction Rates

Relevance to other Lecture Courses

Kinetics and Mechanism
Modern Liquid Kinetics
Interfacial Kinetics
Photochemistry and Energy Transfer
Atmospheric Chemistry
Dynamics of Molecular Collisions

Dr M. BROUARD A) BIMOLECULAR REACTION RATES

8 Lectures 1) **Why bother?**

$$k(T) = A e^{-E_a/RT} \quad (1)$$

- What determines the magnitudes of A and E_a ?
- Can these parameters be calculated *a priori*?
- When (and why) does equation 1 break down?

5 Lectures

3 Lectures



Simple Collision Theory (SCT)

(Pilling and Seakins, p61 box 3.1) Z_{AB}^0 is the *collision number*

Key ideas

- Reactions occur by collisions¹
- Collision energy² (E_t) must exceed the barrier height (E_0)

$$Z_{AB}^0 = \bar{c}_{\text{rel}} \sigma_c \quad \bar{c}_{\text{rel}} = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2}$$

and

$$\sigma_c = \pi d^2$$

is the *collision cross-section*.

Reaction rate = Collision rate \times fraction of collisions with $E_t > E_0$

Reaction rate

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

Fraction of collisions with $E_t > E_0$

$$e^{-E_0/RT}$$

Collision rate

$$Z_{AB}^0 [A] [B]$$

The *thermal* rate coefficient is therefore

¹Reactants are structureless spheres, with radii r_A and r_B and collision diameter $d = r_A + r_B$

²The collision energy is the translational energy associated with *relative motion*

$$E_t = \frac{1}{2} \mu c_{\text{rel}}^2 \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

where c_{rel} is the relative speed ($c_{\text{rel}} = v_B - v_A$).

$$k_{SCT}(T) = \bar{c}_{\text{rel}} \sigma_c e^{-E_0/RT} \quad (2)$$

$$A_{\text{SCT}} = \bar{c}_{\text{rel}} \sigma_c$$

Need to think about reactive collisions in more detail.

Reaction	T/K	$E_a/\text{kJ mol}^{-1}$	$10^{-11} A_{\text{expt}}/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	$10^{-11} A_{\text{sct}}/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	P
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	600	0	10.0	2.1	4.8
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	300	0	0.24	1.1	0.22
$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$	470	102	0.094	0.59	0.16
\rightarrow	500	83	1.5×10^{-5}	3.0	5.0×10^{-5}
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	800	180	1.2×10^{-5}	7.3	1.7×10^{-6}

POTENTIAL ENERGY SURFACE

FORCES ON NUCLEI

MOTIONS OF NUCLEI

Implies the *reaction* cross-section, σ_r , might be better written

$$\sigma_r = P \sigma_c$$

where P is the probability of reaction on collision or the *steric factor*.

CLASSICAL MECHANICS

QUANTUM MECHANICS

simple collision theory

transition state theory

³In the table of data the activation energies have been experimentally determined using

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (3)$$

The collision cross-sections $\sigma_c = \pi d^2$ are taken from viscosity data.

Collisions between two Atoms and Potential Energy Curves
(See Valence Lectures)

Separate the electronic and nuclear motions of atoms A and B (Born-Oppenheimer approximation)

$$\psi_{\text{tot}}(r, R) = \psi_{\text{el}}(r; R)\psi_{\text{n}}(R)$$

Solve the Schrödinger equation for the electronic motion

$$\hat{H}_{\text{e}}\Psi_{\text{e}} = V(R)\Psi_{\text{e}}$$

Force, $F(R)$, acting on the particles at separation R

$$F(R) = -\frac{dV(R)}{dR}$$

For specified initial positions and velocities of the atoms, their motion during the collision is calculated classically using Newton's Laws.

The *potential energy curve*, $V(R)$, for an electronic state is the dependence of the electronic energy on A-B nuclear separation, R .

$$\hat{H}_{\text{n}}\psi_{\text{n}}(R) = E_{\text{n}}\psi_{\text{n}}(R)$$

$$E_{\text{n}} = h\nu(v + \frac{1}{2}) + \dots$$

Head on collision

Below the dissociation limit the vibrational levels of AB can be calculated from $V(R)$ (see J.M Brown, *Molecular Spectroscopy Primer*).

Glancing blow collisions

Collisions between molecules and Potential Energy Surfaces

For the simplest chemical reaction



the potential energy will depend on three coordinates, (r_1, r_2, θ) ,

b is known as the *impact parameter* (defined as the distance of closest approach of the atoms in the absence of an interaction potential)

It determines the magnitude of the *orbital angular momentum* of the collision⁴

The resulting potential energy function, or *surface*, has the following form, plotted as a function of r_1 and r_2 at two fixed values of the bond angle θ :

$$|\ell| = \mu_{\text{rel}} b$$

In the absence of a third species, which could remove the excess energy and stabilize the AB molecule *via* a secondary collision, only *elastic scattering* occurs in an atom-atom collision.

⁴Quantum mechanically the orbital angular momentum $|\ell| = \hbar\sqrt{L(L+1)}$.

Reaction Coordinate and the Reaction Barrier

The reaction coordinate is the *minimum potential energy pathway* (MEP) from reactants to products.

The PES provides information on the barrier height to reaction. Vibrational force constants and vibrational frequencies can also be determined (see lectures 3 and 4).

The potential energy barrier, V^\ddagger , is the maximum potential energy along the reaction coordinate.⁵

The barrier is a saddle point on the potential energy surface, and may be thought of as a bottleneck through which reactants must pass if they are to proceed to form products.

As with atom-atom collisions, once the potential energy surface (PES) is known, the forces on the particles can be calculated (lecture 2).

⁵ V^\ddagger is sometimes referred to as the *classical barrier height* because it does not include vibrational zero-point energy (see lectures 2 and 3)

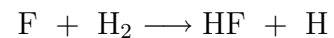
2) Molecular Collisions

Types of Potential Energy Surface

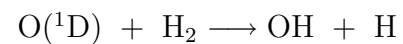
Classical motion over the potential energy surface

Solving the classical laws of motion for a set of initial conditions (the initial positions and velocities or momenta of each atom) yields the *classical trajectory* of the particles.

Direct reactions with barriers



Reactions with deep potential energy wells (lectures 6 to 8)



The two trajectories, shown in different ways in the figures above and below, represent examples of an *inelastic* (energy transfer) collision and a *reactive* collision:

The Reaction Probability

Not all collisions lead to reaction.

Collisions with different angles of approach, γ , and impact parameters, b , have different probabilities of reaction, $P(b, \gamma)$.

In practice, many ($\sim 10^6$) trajectories, corresponding to different initial conditions, are needed to obtain accurate value for $k(T)$.⁶

⁶This method of calculating $k(T)$ is usually referred to as the *classical trajectory method*.

(See Pilling and Seakins p65 for a modified version of simple collision theory which accounts for the angle dependence of the reaction barrier.)

Reaction Cross-sections

The reaction cross-section can be expressed as an integral of the reaction probability over impact parameter.

$$\sigma_r = \int_0^{b_{\max}} P(b) 2\pi b \, db . \quad (4)$$

$P(b)$, is known as the *opacity function*. It can be calculated using the classical trajectory method, by running trajectories at different impact parameters.

$$P(b) = \frac{N_{\text{reactive}}(b)}{N_{\text{total}}(b)}$$

Head-on collisions tend to be more reactive than glancing-blow collisions.

Cross-section dependence on collision energy

Reaction cross-sections usually vary with collision energy, ϵ_t .

For a reaction with a barrier, collisions at high collision energy are more reactive than those at low collision energy

The rate constant for a reaction should therefore be obtained from reaction cross-sections by evaluating the Maxwell-Boltzmann average of $c_{\text{rel}} \sigma_r(\epsilon_t)$:

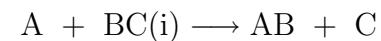
$$k(T) = \int_0^{\infty} c_{\text{rel}} \sigma_r(\epsilon_t) f(\epsilon_t) \, d\epsilon_t$$

(See Pilling and Seakins pp 61-65)

Cross-section dependence on rovibrational state

Trajectories over two different surfaces illustrating that the reaction cross-sections can also depend on the reactant molecule vibrational (and rotational) state.

State-specific to thermal rate constants



The thermal rate constant may be written as a reactant Boltzmann population (P_i) weighted sum over state-specific rate constants, $k_i(T)$:

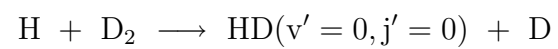
$$k(T) = \sum_i P_i k_i(T) \quad (5)$$

An example of a reaction showing strong vibrationally dependent reaction rate constants will be discussed in lecture 4.

The reaction barrier is a bottleneck through which trajectories must pass if products are to be formed: motion of the reactants along specific coordinates is required if reaction is to occur.

A Reaction Movie

A quantum mechanical movie of a reaction taking place
(Althorpe J. Chem. Phys. **114** 1601 (2001))



(See 3rd Year Lectures on the Dynamics of Molecular Collisions)

3) Transition State Theory⁷

The Reaction Coordinate



Why develop an approximate theory?

- Rigorous QM calculations only possible for $N \leq 4$
- For $N \geq 4$ classical trajectory calculations are also time-consuming
- Both require knowledge of the full Potential Energy Surface
- Simple collision theory doesn't work

The key advantage with *transition state theory* is that you only need to know the PES at the *transition state*.

⁷Simpler derivations of transition state theory which employ the *quasi-equilibrium hypothesis* appear in many of the recommended texts (e.g., Pilling and Seakins, p66), and in the 'Applications of Statistical Mechanics' lecture course next year.

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 the barrier.

REACTION IN ONE DIMENSION

Thus, the rate constant in one dimension is

$$k(T) = \int_0^{\infty} P(\epsilon_t) c f(c) dc$$

This can be written in terms of kinetic energies

$$k(T) = \int_0^{\infty} P(\epsilon_t) f(\epsilon_t) \frac{d\epsilon_t}{\mu}$$

where $\epsilon_t = \frac{1}{2}\mu c^2$,

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

and q_t is a 1D translational partition function *per unit length*:

$$q_t = \left(\frac{2\pi\mu kT}{h^2} \right)^{1/2} \quad \text{with } \mu = \frac{m_A m_{BC}}{m_A + m_{BC}}$$

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

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

where $f(c)$ is the 1-D Maxwell-Boltzmann distribution of relative velocities.

The reaction rate is the approach rate times the probability of reaction at a given collision energy, $P(\epsilon_t)$

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

Hence the thermally averaged reaction rate is

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

q_t represents the number of thermally accessible translational states per unit length at temperature, T .

Substitution into the expression for $k(T)$ yields⁸

$$k(T) = \frac{1}{h q_t} \int_0^{\infty} P(\epsilon_t) e^{-\epsilon_t/kT} d\epsilon_t \quad (6)$$

⁸Note that equation 6 is dimensionally correct for a rate constant in 1D (m molecule⁻¹ s⁻¹).

REACTION (A+BC) IN MANY DIMENSIONS

A and BC approach in specific quantum states - equation 6 applies to each quantum state, weighted by the Boltzmann population for the molecules in those states:

$$k(T) = \frac{1}{h q_t} \int_0^\infty \sum_n P_n(\epsilon_t) \frac{g_n e^{-\epsilon_n/kT}}{q_{A:int} q_{BC:int}} e^{-\epsilon_t/kT} d\epsilon_t \quad (7)$$

where g_n is the degeneracy of state n , and ⁹

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

with

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

⁹The internal partition function for atom A is simply the electronic partition function, which is usually just given by the electronic degeneracy of the ground state.

This equation is usually written more compactly as:

$$k(T) = \frac{1}{h q} \int_0^\infty N(\epsilon) e^{-\epsilon/kT} d\epsilon \quad (8)$$

where

$$N(\epsilon) = \sum_n g_n P_n(\epsilon) \quad \text{with} \quad \epsilon = \epsilon_t + \epsilon_n ,$$

and q is the total reactant partition function ($q_t q_{A:int} q_{BC:int}$).

$N(\epsilon)$ is called the *cumulative* reaction probability¹⁰.

Equations 7 and 8 are *exact* provided the reactants are in thermal equilibrium.

¹⁰The sum of reaction probabilities $N(E)$ includes reactant orbital angular momentum quantum states, labeled with quantum number L with degeneracy $2L + 1$. In transition state theory this motion is accounted for *via* the rotational partition function of the transition state.

The Transition State

The Transition State Theory expression for $k(T)$

Transition state theory provides an approximate expression for $N(\epsilon)$.

The transition state is a bottleneck on the PES through which reactants must pass if they are to form products.¹¹

From assumption 2 the total energy at the transition state may be written

$$\epsilon = \epsilon_t^\ddagger + \epsilon_n^\ddagger + \epsilon_0$$

The assumptions of transition state theory are:

1. The reactants are in thermal equilibrium (as assumed in the preceding section)
2. Motion along the minimum energy path is separable from motion orthogonal to it
3. Motion along reaction coordinate is classical
4. Motion along the minimum energy path is direct. (This is often referred to as the *no re-crossing* rule - see K. Laidler p116.)

ϵ_0 is the *difference in zero-point energies* between the reactant and transition state.

Assumptions 3 and 4 imply

$$P_n(\epsilon_t^\ddagger) = 1 \quad \text{if } \epsilon_t^\ddagger > 0$$

¹¹It is formally defined as a *dividing surface* on the PES separating reactants from products, and is usually located at the top of the barrier

Substitution into equation 7, changing the variable of integration to ϵ_t^\ddagger , *Recombination of two atoms - simple collision theory revisited*¹³ yields

$$k(T) = \frac{\sum_n g_n^\ddagger e^{-\epsilon_n^\ddagger/kT}}{h q_t q_{A:\text{int}} q_{BC:\text{int}}} e^{-\epsilon_0/kT} \int_0^\infty e^{-\epsilon_t^\ddagger/kT} d\epsilon_t^\ddagger \quad (9) \quad A + B \longrightarrow AB^\ddagger \longrightarrow \text{products}$$

Evaluating the integral over translational energies yields

$$k(T) = \frac{kT}{h} \frac{q_{\text{int}}^\ddagger}{q_t q_{A:\text{int}} q_{BC:\text{int}}} e^{-\epsilon_0/kT} \quad (10)$$

For the transition state

$$q_{\text{int}}^\ddagger = q_{\text{rot}}^\ddagger = \frac{kT}{B^\ddagger}$$

where¹²

$$q_{\text{int}}^\ddagger = q_{\text{rot}}^\ddagger q_{\text{vib}}^\ddagger q_{\text{el}}^\ddagger \quad \text{and} \quad q_t = \left(\frac{2\pi\mu kT}{h^2} \right)^{3/2} \equiv \left[\frac{q_t^\ddagger}{q_{A:t} q_{BC:t}} \right]^{-1} \quad B^\ddagger = \frac{h^2}{8\pi^2\mu d^2} \quad \text{where } d = r_A + r_B$$

and

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

The single ‘vibrational’ mode of AB^\ddagger is the reaction coordinate, and hence is *not* included in q_{int}^\ddagger .

For the reactants

$$q_t = \left(\frac{2\pi\mu kT}{h^2} \right)^{3/2} \equiv \left[\frac{q_t^\ddagger}{q_{A:t} q_{BC:t}} \right]^{-1} \quad \text{and} \quad q_{A/B:\text{int}} = 1$$

In terms of the total molecular partition functions of the transition state and reactant molecules this expression can be rewritten more simply

$$k(T) = \frac{kT}{h} \frac{q^\ddagger}{q_A q_{BC}} e^{-\epsilon_0/kT} \quad (11)$$

Substitution into equation 10 yields

$$k(T) = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \pi d^2 e^{-\epsilon_0/kT} \quad (12)$$

This is the same expression as simple collision theory.

$k(T)$ has units of $\text{m}^3 \text{molecule}^{-1} \text{s}^{-1}$.

¹²Note that q_{vib}^\ddagger *excludes* the ‘vibrational’ or ‘translational’ degree of freedom corresponding to motion along the reaction coordinate.

¹³For the reaction to occur, the excited AB product must be stabilized by collisions with a high pressure of an added bath gas - see lectures 6 - 8.

Summary of expressions for partition functions

Motion	Symbol	Degrees of Freedom	Partition Function	Order of Magnitude
Translation	$q_{A:t}$	3	$\left(\frac{2\pi m_A k_B T}{h^2}\right)^{3/2}$	$10^{30} - 10^{33} \text{ m}^{-3}$
Rotation (Linear)	$q_{BC:rot}$	2	$\frac{k_B T}{\sigma h c B}$	$10^1 - 10^2$
Rotation (Non-linear)	$q_{ABC:rot}$	3	$\frac{1}{\sigma} \left(\frac{k_B T}{hc}\right)^{3/2} \left(\frac{\pi}{ABC}\right)^{1/2}$	$10^2 - 10^3$
Vibration (Linear)	$q_{ABC:vib}$	$3N - 5$	$\prod_i^{3N-5} q_{vib}^i$	1-10
Vibration (Non-linear)	$q_{ABC:vib}$	$3N - 6$	$\prod_i^{3N-6} q_{vib}^i$	1-10
TS Vibration (Linear)	q_{vib}^\ddagger	$3N - 6$	$\prod_i^{3N-6} q_{vib}^i$	1-10
TS Vibration (Non-linear)	q_{vib}^\ddagger	$3N - 7$	$\prod_i^{3N-7} q_{vib}^i$	1-10
Electronic	$q_{BC:el}$	—	$\sum_i g_i e^{-\epsilon_i/k_B T}$	g_0

$$q_{vib}^i = (1 - e^{-hc\nu_i/k_B T})^{-1}$$

Rotational constants, A,B and C, and vibrational frequencies, ν , expressed in cm^{-1} .

4) Applications of Transition State Theory

Detailed calculation of thermal rate constant

Estimating the Steric Factor

TST can be used to estimate the steric factor.

TST for $A + B \rightarrow AB$ is the same as SCT (lecture 3)

$$k_{\text{sct}}(T) \sim \frac{kT}{h} \frac{q_{\text{rot}}^2}{q_{\text{t}}^3} e^{-\epsilon_0/kT}$$

Here the partition functions have been re-defined as partition functions per degree of freedom, (i.e. $q_{\text{rot}}^2 = (kT/\sigma B^\ddagger)$).

For $AB + CD \rightarrow ABCD^\ddagger \rightarrow$ products proceeding *via* a non-linear $ABCD^\ddagger$ transition state

$$k_{\text{tst}}(T) \sim \frac{kT}{h} \frac{q_{\text{rot}}^3 q_{\text{vib}}^5}{q_{\text{t}}^3 q_{\text{rot}}^4 q_{\text{vib}}^2} e^{-\epsilon_0/kT}$$

The steric factor is

$$p = \frac{k_{\text{tst}}(T)}{k_{\text{sct}}(T)} \sim \left(\frac{q_{\text{vib}}}{q_{\text{rot}}} \right)^3$$

Using the order of magnitude estimates of the partition functions (lecture 3)

$$p = \left(\frac{q_{\text{vib}}}{q_{\text{rot}}} \right)^3 \sim 10^{-2} - 10^{-4}$$

Generally, the estimated steric factor falls with increasing reactant complexity.



$$k(T) = \frac{kT}{h} \frac{q_{\text{int}}^\ddagger}{q_{\text{t}} q_{\text{H:int}} q_{\text{D}_2:\text{int}}} e^{-\epsilon_0/kT}$$

The transition state is linear.

Parameter	Reactants (D ₂)	Transition State
$r_{\text{e,HD}}/\text{\AA}$	—	0.93
$r_{\text{e,DD}}/\text{\AA}$	0.741	0.93
Potential energy $V^\ddagger/\text{kJ mol}^{-1}$	0.0	39.91
Frequencies/ cm^{-1}		
Stretch	3109	1762
Bend (doubly degenerate)	—	694

At 300 K:

$$\begin{aligned}
 \epsilon_0 &= V^\ddagger + \epsilon_z^{\text{HDD}} - \epsilon_z^{\text{DD}} \\
 &= 39.91 + 18.84 - 18.59 = 40.16 \text{ kJ mol}^{-1} \\
 e^{-\epsilon_0/k_B T} &= 1.02 \times 10^{-7} \\
 \frac{k_B T}{h} &= 6.25 \times 10^{12} \text{ s}^{-1} \\
 q_t &= \left(\frac{2\pi\mu k_B T}{h^2} \right)^{3/2} = 6.99 \times 10^{29} \text{ m}^{-3}
 \end{aligned}$$

For the transition state

$$\begin{aligned}
 I^\ddagger &= \frac{m_1 m_2 + 4m_1 m_3 + m_2 m_3}{M} r_e^{\ddagger 2} = 4.02 \times 10^{-47} \text{ kg m}^2 \\
 B^\ddagger &= \frac{\hbar^2}{2I^\ddagger} = 1.38 \times 10^{-22} \text{ J molecule}^{-1} \\
 q_{\text{rot}}^\ddagger &= \frac{k_B T}{B^\ddagger} = 30.0 \\
 q_{\text{vib}}^\ddagger &= \prod_i (1 - e^{-h\nu_i/k_B T})^{-1} = 1.0002 \cdot (1.037)^2 = 1.076
 \end{aligned}$$

For the reactants¹⁴

$$\begin{aligned}
 I_{\text{D}_2} &= 9.14 \times 10^{-48} \text{ kg m}^2 \\
 B_{\text{D}_2} &= \frac{\hbar^2}{2I_{\text{D}_2}} = 6.08 \times 10^{-22} \text{ J molecule}^{-1} \\
 q_{\text{D}_2:\text{rot}} &= \frac{k_B T}{2B} = 3.41 \\
 q_{\text{D}_2:\text{vib}} &= (1 - e^{-h\nu/k_B T})^{-1} = 1.00
 \end{aligned}$$

Substitution into the expression for $k(T)$ yields

$$\begin{aligned}
 k(T) &= 8.46 \times 10^{-17} e^{-\epsilon_0/k_B T} \\
 &= 8.63 \times 10^{-24} \text{ m}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
 &\equiv 8.63 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
 \end{aligned}$$

	$k(T = 300 \text{ K})/10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Experimental	2.1
Transition state theory	0.86
Quantum mechanics	1.9
Classical mechanics	1.8

¹⁴The assumption that one can employ the high temperature expression for the rotational partition functions leads to a relatively small error at 300 K

The discrepancy between TST and experiment is due to neglect of tunneling in TST (see below).

Tunneling Corrections

Motion over the barrier cannot always be treated classically

Transmission probability for a square potential energy barrier ¹⁵

$$T = \frac{\psi(b)^2}{\psi(a)^2} \sim e^{-2k(b-a)} \quad k = \sqrt{2\mu(V^\ddagger - \epsilon_t)/\hbar^2}$$

where $b - a$ is the barrier width, V^\ddagger is the barrier height, and ϵ_t is the collision energy.

Tunneling is most important for light particles passing through thin barriers

Tunneling is most apparent at low temperatures.

¹⁵(This is an approximate expression valid when $k(b - a) \gg 1$. See last problem sheet of the Quantum Mechanics lecture course and Atkins and Friedman, *Molecular Quantum Mechanics*)

Failings of Transition State Theory

TST assumes that (the classical) motion along the minimum energy path is direct, i.e. there is no recrossing ¹⁶.

The importance of recrossing trajectories depends on the shape of the potential energy surface, the total energy and the masses of the species involved.

Re-crossing of the transition state is a minor problem at room temperature for reactions with substantial barriers (left figure).

When re-crossing *is* important, TST yields an upper-bound to the classical rate constant.

¹⁶TST also assumes the reactants are in thermal equilibrium. This assumption is generally valid in bulk kinetic studies, where the pressures are sufficiently high to ensure that the rate of inelastic collisions, which serve to restore the system to thermal equilibrium, is greater than the rate of reactive collisions.

Temperature Dependence of rate constants

Consider an A + BC reaction proceeding *via* a linear transition state.

$$k(T) = \frac{kT}{h} \frac{q_{\text{rot}}^{\ddagger}}{q_{\text{t}} q_{\text{BC:vib}} q_{\text{BC:rot}}} e^{-E_0/RT}$$

Assume the vibrational partition functions are unity, and extract the temperature dependence of the rotational and translational partition functions

$$\begin{aligned} k(T) &\simeq C T^1 \frac{T^1}{T^{\frac{3}{2}} T^1} e^{-E_0/RT} \\ &= C T^{-\frac{1}{2}} e^{-E_0/RT} \end{aligned}$$

In general, the temperature dependence of the bimolecular rate constant will have the form

$$k(T) = C T^n e^{-E_0/RT}$$

From the definition of the activation energy, one obtains

$$\frac{d \ln k(T)}{dT} = \frac{nRT + E_0}{RT^2} = \frac{E_a}{RT^2},$$

i.e.

$$E_a = E_0 + nRT$$

Often $E_0 \gg RT$, and the temperature dependence of $k(T)$ is dominated by E_0 .

Non-Arrhenius Behaviour

Tunneling through the reaction barrier can cause curvature in the Arrhenius plot.

The temperature dependence of the partition functions appearing in the A-factor can also cause curvature. This is important when $E_0 \lesssim nRT$, e.g.,¹⁷

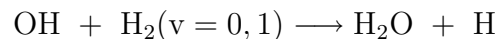


Radical recombination reactions also have $E_0 \sim 0$ - see lectures 6-8)

¹⁷This reaction proceeds *via* an energized HOCO* complex. The unusual temperature dependence arises from the competition between dissociation of HOCO* back to reactants and dissociation to form products. The rate of latter increases rapidly with temperature because the vibrational partition functions for the low frequency vibrational modes of the second transition state increase rapidly with temperature. Tunneling through the second barrier may also be important.

Non-Arrhenius Behaviour

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



Vibrational excitation of the H_2 to $v = 1$ increases the rate constant by over a factor of 100 (i.e. $k_1(T) \gg k_0(T)$).¹⁸

$$k(T) = P_0 k_0(T) + P_1 k_1(T) \quad \text{with} \quad P_v = \frac{e^{-\Delta\epsilon_v/k_B T}}{q_{\text{H}_2:\text{vib}}}$$

The reaction barrier occurs late along the reaction coordinate once the H—H bond is stretched (i.e. the PES has a ‘late barrier’ - see lecture 2).

The curvature for this reaction is reasonably well accounted for by TST once a tunneling correction is made.

¹⁸Vibrational excitation of the ‘spectator’ OH reactant has very little effect on the reaction rate.

Better agreement between TST and experiment can be obtained by varying some of the TS vibrational frequencies. This procedure is often used to extrapolate experimental data to very low or very high temperatures.

Isotope Effects

Transition state theory provides a reliable estimate of the kinetic isotope effect

$$\ln \frac{k_{\text{H}}}{k_{\text{D}}} = \ln \frac{A_{\text{H}}}{A_{\text{D}}} - \frac{E_{\text{aH}} - E_{\text{aD}}}{RT},$$

$E_{\text{aD/H}}$ are the activation energies of the reactions with and without isotopic substitution.

The second term often dominates ($E_{\text{aH}} - E_{\text{aD}} \simeq E_{0\text{H}} - E_{0\text{D}}$).

An upper bound to the kinetic isotope effect may be obtained assuming that the zero point energies of the transition state species are insensitive to isotopic substitution ¹⁹

$$(E_{\text{aH}} - E_{\text{aD}}) \simeq (E_{0\text{H}} - E_{0\text{D}}) \simeq (E_{\text{zD}} - E_{\text{zH}})$$

The difference in activation energies is then approximately the difference in the reactant zero point energies $E_{\text{zH/D}}$.

¹⁹This will be the case if the bond involving the deuterium substitution is significantly weakened in the transition state

5) Thermodynamic Formulation of TST

Thermodynamics

Transition state theory employs partition functions per unit volume²⁰.

Need to express these partition functions in terms of the thermodynamic functions, entropy and enthalpy.

For an ideal gas (see *Statistical Mechanics* Lecture Course and Atkins)

$$S = \frac{U - U(0)}{T} + k \ln Q$$

where $U(0)$ is the internal energy at absolute zero (i.e. the zero-point energy of the N particles) and

$$Q = \frac{q^N}{N!}$$

Here q is the usual (dimensionless) molecular partition function.

The standard molar entropy of an ideal gas can then be written (using Stirling's approximation)

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

Why bother?

$$k(T) = \frac{kT}{h} \frac{q^\ddagger}{q_A q_{BC}} e^{-\epsilon_0/kT}$$

- TS structure and vibrational frequencies may not have been calculated
- For reactions in solution the partition functions are not simply defined (e.g., what about the role of the solvent?)

Is there a simpler expression for $k(T)$ in terms of thermodynamics functions?

²⁰This originates from the fact that rates are proportional to reactant concentrations not reactant partial pressures

For an ideal gas

$$H = U + PV = U + NkT$$

and

$$H(0) \equiv U(0)$$

Therefore the equation for the entropy may be rewritten

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

The partition function *per unit volume* q' and q^\ominus are related by the expression:

$$\frac{q^\ominus}{N_A} = q' \frac{V^\ominus}{N_A} = q' \frac{k_B T}{p^\ominus}$$

and therefore in terms of thermodynamics functions q' can be written ²¹:

$$q' = \frac{q^\ominus}{V^\ominus} = \frac{k_B T}{p^\ominus} e^{S^\ominus/R} e^{-(H^\ominus - H^\ominus(0))/RT} \quad (13)$$

²¹In many kinetics texts, the standard state is taken as unit *concentration* ($c^\ominus = 1.0 \text{ mol dm}^{-3}$). If this convention is used then the same standard state must also be employed when evaluating the thermodynamic functions. Here, however, we will employ the correct thermodynamic standard state of $p^\ominus = 10^5 \text{ Pa}$.

Kinetics

For A + BC reaction in the gas phase (equation 10)

$$k(T) = \frac{kT}{h} \frac{q^\ddagger}{q_A q_{BC}} e^{-\epsilon_0/kT}$$

Multiplying this equation by N_A converts $k(T)$ into units of $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Then, using $N_A \epsilon_0 \equiv \Delta^\ddagger U^\ominus(0)$ and equation 13 (dropping the primes) ²²

$$k(T) = \frac{RT}{p^\ominus} \frac{kT}{h} e^{\Delta^\ddagger S^\ominus/R} e^{-\Delta^\ddagger H^\ominus/RT} \quad (14)$$

$\Delta^\ddagger H^\ominus$ Enthalpy of activation

$\Delta^\ddagger S^\ominus$ Entropy of activation

Note that $k(T)$ has the units of $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and the standard state for evaluating $\Delta^\ddagger H^\ominus$ and $\Delta^\ddagger S^\ominus$ is $p^\ominus = 10^5 \text{ Pa}$ above).

²²This equation can be rewritten

$$k(T) = \frac{RT}{p^\ominus} \frac{kT}{h} e^{-\Delta^\ddagger G^\ominus/RT}$$

i.e. (given $\Delta G^\ominus = -RT \ln K$)

$$k(T) = \frac{RT}{p^\ominus} \frac{kT}{h} K^\ddagger$$

This suggests the alternative derivation of equation 14 (found in most texts), which is based on the (questionable) assumption of a *quasi-equilibrium* between reactants and transition state



Comparison with the Arrhenius equation

For a bimolecular reaction involving ideal gases

$$\Delta^\ddagger H^\ominus = \Delta^\ddagger U^\ominus + \Delta n RT$$

with $\Delta n = -1$.

The activation energy is calculated from

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

by substituting the TS expression for $k(T)$

$$k(T) = \frac{RT}{p^\ominus} \frac{k_B T}{h} e^{\Delta^\ddagger S^\ominus / R} e^{-\Delta^\ddagger H^\ominus / RT}$$

This yields

$$E_a = \Delta^\ddagger H^\ominus + 2RT$$

or

$$\Delta^\ddagger H^\ominus = E_a - 2RT$$

Thus

$$k(T) = e^2 \frac{RT}{p^\ominus} \frac{k_B T}{h} e^{\Delta^\ddagger S^\ominus / R} e^{-E_a / RT} . \quad (15)$$

The entropy of activation

$$\Delta^\ddagger S^\ominus = S^\ominus_{\ddagger} - S^\ominus_A - S^\ominus_{BC}$$

where S^\ominus_{\ddagger} is the entropy of the transition state ²³

The entropy of activation represents the change in entropy in going from the reactants to the transition state.

For gas phase *bimolecular* reactions $\Delta^\ddagger S^\ominus < 0$, reflecting the loss of translation entropy on forming a single transition state species from two separate reactants.

The A-factor from simple collision theory (lectures 3+4) yields an entropy of activation of about $-50.0 \text{ J K}^{-1} \text{ mol}^{-1}$.

More negative values (reflecting a larger *decrease* in entropy on forming the TS) imply a lower A-factor than predicted by simple collision theory.

²³ S^\ominus_{\ddagger} excludes the entropy associated with motion along the reaction coordinate.

[Aside]

For unimolecular reactions in the gas phase (in the high pressure limit - see Lectures 6-8), an analogous derivation yields

$$k(T) = e^1 \frac{kT}{h} e^{\Delta^\ddagger S^\ominus / R} e^{-E_a / RT} \quad (16)$$

For activation controlled *solution phase* reactions (see Modern Liquid Kinetics lecture course and Pilling and Seakins, pp155-156), either equation 16 is employed, or the equivalent expression²⁴

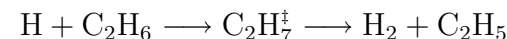
$$k(T) = \frac{1}{c^\ominus} \frac{kT}{h} e^{\Delta^\ddagger S^\ominus / R} e^{-\Delta^\ddagger H^\ominus / RT} \quad (17)$$

where c^\ominus is usually taken as 1.0 mol dm^{-3} , and at constant pressure

$$\Delta^\ddagger H^\ominus = \Delta^\ddagger U^\ominus + P \Delta^\ddagger V^\ominus \sim \Delta^\ddagger U^\ominus$$

In solution, the thermodynamic functions of activation in these expressions *include* the entropic and enthalpic terms associated with encounter pair formation.

²⁴However, note that for solutions, the equations for the canonical and molecular partition functions employed in the preceding sections are no longer valid, and equation 17 is written down more by analogy with the gas phase expressions.



Estimate the A -factor for this gas phase reaction reaction at 400 K.

Use C_2H_6 as a ‘model’ on which to base calculation of S_{\ddagger}^\ominus (i.e. S^\ominus for $\text{C}_2\text{H}_7^\ddagger$).

$$\Delta^\ddagger S^\ominus = S_{\ddagger}^\ominus - S_{\text{H}}^\ominus - S_{\text{C}_2\text{H}_6}^\ominus$$

1. Translational Contribution to S_{\ddagger}^\ominus

$$m_{\text{C}_2\text{H}_6} \simeq m_{\text{C}_2\text{H}_7}$$

$$S_{\ddagger:\text{trans}}^\ominus \simeq S_{\text{C}_2\text{H}_6:\text{trans}}^\ominus$$

2. Rotational Contribution

$$I_{\text{C}_2\text{H}_6} \simeq I_{\text{C}_2\text{H}_7}$$

Reduction in symmetry on forming the TS (symmetry numbers)

$$\sigma_{\text{C}_2\text{H}_6} = 6 \sigma_{\text{C}_2\text{H}_7}$$

Thus

$$S_{\ddagger:\text{rot}}^\ominus \simeq S_{\text{C}_2\text{H}_6:\text{rot}}^\ominus + R \ln 6$$

3. Vibrational Contribution

Neglect changes in vibrational and internal rotational partition functions on forming the H—H—C structure.

$$S_{\ddagger:\text{vib}}^\ominus \gtrsim S_{\text{C}_2\text{H}_6:\text{vib}}^\ominus$$

4. Electronic Contribution

C_2H_6 has a singlet ground state, that of $C_2H_7^\ddagger$ will be a doublet

$$S_{\ddagger:el}^\ominus \simeq S_{C_2H_6:el}^\ominus + R \ln 2$$

A lower limit for the entropy of the TS is therefore

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

5. H atom Entropy

S_H^\ominus is obtained from the Sackur-Tetrode equation²⁵

6. Entropy of Activation

A lower limit on the entropy of activation is therefore

$$\Delta^\ddagger S^\ominus = S_{\ddagger}^\ominus - S_H^\ominus - S_{C_2H_6}^\ominus \gtrsim -100.06 \text{ J K}^{-1} \text{ mol}^{-1}$$

7. The A-factor

A lower limit for the A-factor is

$$A = e^2 \frac{RT}{p^\ominus} \frac{k_B T}{h} e^{\Delta^\ddagger S^\ominus / R}$$

$$A \geq 1.2 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \equiv 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

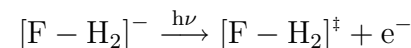
The experimental A-factor is $1.0 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (i.e. within a factor of 10).

²⁵Note that H is a ²S atom and that the standard state is 10^5 Pa .

Observing the Transition State Region.

Photoelectron spectroscopy of FH_2^-

Measure the kinetic energies of the ejected photoelectrons



The neutral products are produced in geometries very close to those of the transition state for the reaction

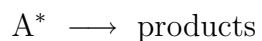
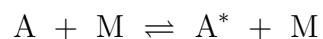


The spectrum suggests that the transition state is bent (see Science, **262**, (1993), 1852).

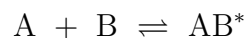
B) UNIMOLECULAR REACTION RATES

Relevance

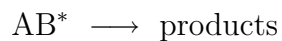
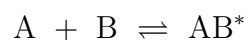
(i) *Thermal Unimolecular Reactions*



(ii) *Radical Recombination*



(iii) *Chemical Activation*



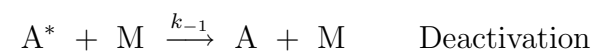
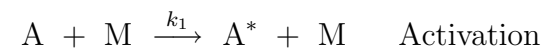
(iii) *Photodissociation*



See *Photochemistry* lectures

6) Thermal Unimolecular Reactions

The Lindemann Mechanism



M is a 'third body' - another gas molecule in the system.

$$-\frac{d[A]}{dt} = k_2[A^*] = k_{\text{uni}}[A]$$

i.e.

$$k_{\text{uni}} = \frac{[A^*]}{[A]} k_2$$

Steady state approximation

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

The phenomenological unimolecular rate constant is

$$k_{\text{uni}} = \frac{[A^*]}{[A]} k_2 = \left[\frac{k_1[M]}{k_{-1}[M] + k_2} \right] k_2 \quad (18)$$

Plots of the variation of k_{uni} with pressure are known as the *fall-off curve*.

Limitations with Lindemann Theory

(i) Equation 18 may be rearranged

$$\frac{1}{k_{\text{uni}}} = \frac{1}{k_{\infty}} + \frac{1}{k_1[M]} \quad (19)$$

Thus a plot of $1/k_{\text{uni}}$ versus $1/[M]$ should be linear with slope $1/k_1$ and intercept $1/k_{\infty}$.

(i) Limiting High Pressures ($k_{-1}[M] \gg k_2$)

$$k_{\text{uni}} = k_{\infty} = \frac{k_1}{k_{-1}} k_2$$

(ii) Limiting Low Pressures ($k_{-1}[M] \ll k_2$)

$$k_{\text{uni}} = k_0 = k_1[M]$$

Qualitatively agrees with experiment (a good thing)

(ii) $[M]_{1/2}$ is the concentration (proportional to pressure) at which $k_{\text{uni}} = k_{\infty}/2$. From equation 19

$$[M]_{1/2}^{\text{calc}} = \frac{k_{\infty}}{k_1}$$

Fix k_{∞} to the experimental value.

Use simple collision theory to calculate k_1

$$k_1 = pZ_{\text{AM}}^0 e^{-\epsilon_0/kT} \quad (20)$$

where ϵ_0 is the energy threshold to reaction (the critical energy) and $Z_{\text{AM}}^0 = c_{\text{rel}}^- \sigma_c$ (the collision number).

Different unimolecular reactions have different minimum energy pathways.

Isomerization

Elimination

Bond fission

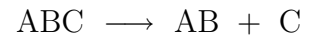
How does the molecule receive and loose energy (energy transfer)?

What is an energized molecule - how does it behave?

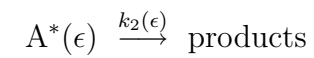
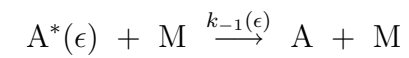
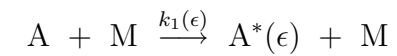
How does the energized molecule react?

Suggests $p \sim 10^8 \gg 1$ (activation is much more efficient than expected).

Potential Energy Surfaces



The Energy Dependent Lindemann Scheme



Apply the steady state approximation $A^*(\epsilon)$

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

Seems likely that k_2 will increase with energy.

Compare with equation 18

Deactivation - the Strong Collision Assumption

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

Strong collisions

Assume every collision renders $A^*(\epsilon)$ unreactive

$$k_{-1}(\epsilon) = Z_{AM}^0$$

Contribution to k_{uni} at energy ϵ is $n(\epsilon) k_2(\epsilon)$

Weak Collisions

$$k_{uni} = \int_{\epsilon_0}^{\infty} n(\epsilon) k_2(\epsilon) d\epsilon \quad (21)$$

Better to treat activation-deactivation in a step-ladder fashion. Critical parameter is average energy transferred per collision $\langle \Delta E^2 \rangle^{1/2}$

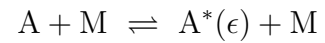
where $n(\epsilon)d\epsilon$ is the fraction of A molecules in the energy range $\epsilon \rightarrow \epsilon + d\epsilon$.

Bath gas	He	Xe	H ₂ O	C ₃ H ₈
$\langle \Delta E^2 \rangle^{1/2} / \text{cm}^{-1}$	215	320	820	880

Efficiency of deactivation increases with increasing complexity of molecule.

Problems to address

In the high pressure limit there is a rapid pre-equilibrium



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

What are the degeneracies (or *density of states*) $g(\epsilon)$? (lecture 8)

As the pressure is decreased, the equilibrium between A^* and A is perturbed by the reaction.

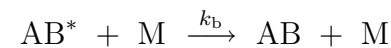
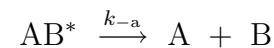
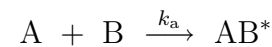
The most highly excited A^* molecules are preferentially depleted by reaction (they have bigger k_2).

If $n(\epsilon)$ changes with pressure, k_{uni} is likely to as well (equation 21).

7) Energy Dependent Reaction Rates

Chemical Activation

Radical recombination



$$-\frac{d[A]}{dt} = k_{\text{rec}}[A][B]$$

Using steady state approximation for AB^* yield

$$k_{\text{rec}} = \frac{k_a k_b [M]}{k_{-a} + k_b [M]}$$

(i) Low pressure

$$k_{\text{rec}} = \frac{k_a k_b}{k_{-a}} [M] \quad 3^{\text{rd}} \text{ order kinetics}$$

(ii) High pressure

$$k_{\text{rec}} = k_a \quad 2^{\text{nd}} \text{ order kinetics}$$

Formal reverse of a bond fission unimolecular reaction

$$K_c = \frac{k_{\text{rec}}}{k_{\text{uni}}}$$

Evidence for the Energy Dependence Reaction Rates

Chemical Activation studies

(i) The isomerization of methylcyclopropane

$$\text{Reaction rate} = \frac{d[\text{C}]}{dt} = k_c[\text{AB}^*]$$

$$\text{Stabilization rate} = \frac{d[\text{AB}]}{dt} = k_b[\text{M}][\text{AB}^*]$$

$$\frac{\text{Reaction rate}}{\text{Stabilization rate}} = \frac{[\text{C}]}{[\text{AB}]} = \frac{k_c}{k_b[\text{M}]}$$

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

Choose process with small k_{-a}

a) The total reaction rate to produce the mixture of butenes *increases* with energy in AB^*

b) The composition of the butene mixture is *independent* of the source of the energized molecule

Implies rapid randomization (or flow) of energy within AB^* on a timescale shorter than that for reaction

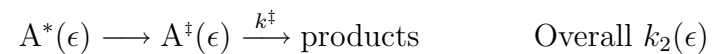
Vary lifetime of AB^* by changing $[\text{M}]$

(ii) The dissociation of bicyclopropyl derivatives

The reaction rate constant, $k_2(\epsilon)$ (Pilling and Seakins, pp 126-128)

Illustrate ideas with *RRK theory* for unimolecular reactions

Distinguish between *energized molecule*, $A^*(\epsilon)$, and the *activated molecule*, A_m^\ddagger



- a) At pressures ≤ 310 Torr, the product ratio I/II is invariant to pressure
($\equiv [M]$)
b) At much higher pressures, product I dominates

Timescale for energy flow (or *intramolecular vibrational redistribution* or *IVR*) $\sim 10^{-12}$ s.

IVR (or vibrational energy flow) is usually much more rapid than reaction

- Ignore A^* rotation
- Molecule A has s identical *harmonic* oscillators with energy ϵ
- $A^\ddagger(\epsilon)$ also has s identical oscillators, but energy ϵ_0 is localized in one vibrational mode, the reaction coordinate
- A^\ddagger falls apart with rate constant k^\ddagger (of the order of an inverse vibrational period ($\sim 10^{-13}$ s)) independent of energy
- Vibrational energy flows freely in the energized and activated species

RRK theory is a *statistical theory* of unimolecular reactions.

If energy flow is rapid and random (i.e. unrestricted or *free*), the vibrational energy in A^* will be distributed statistically²⁶.

Statistically, the fraction of A^* molecules with energy ϵ_0 localized in one bond (the reaction coordinate) is

$$r^\ddagger(\epsilon) = \left(\frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1}$$

Thus

Reaction Rate constant

$$k_2(\epsilon) = k^\ddagger \frac{[A^\ddagger(\epsilon)]}{[A^*(\epsilon)]} = k^\ddagger r^\ddagger(\epsilon) \quad (22)$$

$$k_2(\epsilon) = k^\ddagger \left(\frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1} \quad \epsilon \geq \epsilon_0 \quad (23)$$

r^\ddagger is the fraction of energized molecules which have energy ϵ_0 localized in the reaction coordinate

²⁶In this context statistical means that each microstate of the system at fixed energy is equally accessible. The microstate refers to a specific way of distributing the vibrational energy among the s oscillators (see lecture 8).

Interpretation of $k_2(\epsilon)$

How does an energized molecule behave?

Molecules close to dissociation can be observed spectroscopically

Direct absorption spectroscopy (vibrational overtone spectroscopy)

Emission spectroscopy

A simple statistical interpretation

- As ϵ *increases*, the probability of localizing ϵ_0 in the reaction coordinate also *increases*. Thus $k_2(\epsilon)$ *increases*.
- *Increasing s reduces* the probability that one specific oscillator (the reaction coordinate) receives enough energy, ϵ_0 , for reaction to occur. Thus $k_2(\epsilon)$ *falls*.

When the vibrational energy is low it stays localized in the (nearly harmonic) normal modes

(i) Vibrational Overtone Excitation

As the vibrational energy is raised the motion becomes more *chaotic*

Chaotic motion is induced by the *anharmonicity* of the potential energy surface which couples different vibrational modes ²⁷.

Assumption of rapid IVR on the reaction timescale breaks down for small molecules (because the vibrational motion tends to remain localized and is not chaotic) with small reaction barriers ϵ_0 (since these reactions will be fast).

Best fit parameters:

$$k^\ddagger = 5.98 \times 10^{10} \text{ s}^{-1}$$

$$s = 5$$

$$\epsilon_0 = 11600 \text{ cm}^{-1}$$

from other measurements

²⁷It can also be promoted by coupling between the rotational and vibrational motions of A*

Does RRK theory for $k_2(\epsilon)$ work?

- k^\ddagger and the number of oscillators s need to be adjusted to fit experiment
- s typically takes a value $s \sim \frac{1}{2}(3N - 6)$
- The assumption that all modes are harmonic and have the same frequency does not work
- Rotation can play a role

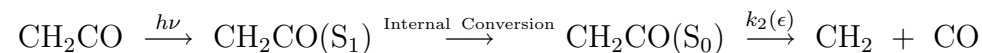
Some of these problems are addressed in a more sophisticated statistical theory called *RRKM theory* (See Pilling and Seakins).

Is the assumption of rapid IVR valid in this case? — Yes...

Both olefinic (CH) and methylenic (CH₂) C—H stretching overtone transitions were employed.

$k_2(\epsilon)$ is *independent* of type of C—H mode excited.

(ii) Flash Photolysis (time-resolved)



The last reaction step is rate determining

The CH₂ product is detected using Laser Induced Fluorescence (LIF)

$k_2(\epsilon)$ is obtained by monitoring the CH₂ LIF intensity as a function of delay time between the ‘pump’, excitation laser pulse, and the ‘probe’ LIF laser pulse.

8) RRK theory and beyond

The activation step and $k_1(\epsilon)$

Pilling and Seakins pp 124-126

Recall (lecture 6) that in the high pressure limit

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

where $g(\epsilon)$ is the vibrational *density of states* (the continuous analogue of degeneracy).

How does the degeneracy arise?

RRK expression for $k_1(\epsilon)$

According to RRK theory (i.e. assuming A^* contains s identical harmonic oscillators)

$$\frac{k_1(\epsilon)}{k_{-1}} = \frac{1}{kT} \frac{1}{(s-1)!} \left(\frac{\epsilon}{kT} \right)^{s-1} e^{-\epsilon/kT} \quad (24)$$

where, within the strong collision approximation, k_{-1} is the collision number, Z_{AM}^0 .

$$\epsilon_{\max} = (s-1) k_B T$$

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

s	ϵ_{\max}	$k_1(\epsilon_{\max})/k_{-1}$
1	0	$1/k_B T$
2	$k_B T$	$0.37/k_B T$
3	$2 k_B T$	$0.27/k_B T$
10	$9 k_B T$	$0.13/k_B T$

Integration of equation 24 over energy yields

$$k_{\text{uni}} = \int_{\epsilon_0}^{\infty} n(\epsilon) k_2(\epsilon) d\epsilon$$

$$\begin{aligned} \frac{k_1}{k_{-1}} &= \int_{\epsilon_0}^{\infty} \frac{k_1(\epsilon)}{k_{-1}} d\epsilon \\ &\simeq \frac{1}{(s-1)!} \left(\frac{\epsilon_0}{kT} \right)^{s-1} e^{-\epsilon_0/kT} \end{aligned} \quad (25)$$

'Steric' factor

$$P = \frac{1}{(s-1)!} \left(\frac{\epsilon_0}{kT} \right)^{s-1}$$

s	P
1	1
2	40
3	810
10	7.8×10^8

$$\epsilon_0 = 100 \text{ kJ mol}^{-1} \text{ and } T = 298 \text{ K.}$$

The expression is only valid in the high pressure limit.

To fit experimental fall-off curves, need to vary s and k^\ddagger .

The RRK expression for k_∞

In the high pressure limit the equation for k_{uni} reduces approximately to the equation

$$\begin{aligned}
 k_\infty &= \int_{\epsilon_0}^{\infty} \frac{k_1(\epsilon)}{k_{-1}} k_2(\epsilon) d\epsilon \\
 &\simeq k^\ddagger e^{-\epsilon_0/kT}
 \end{aligned}
 \tag{26}$$

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

RRK theory provides no means of calculating k^\ddagger *a priori*.

TST for the high pressure limit



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

$$k_\infty = \frac{kT}{h} \frac{q^\ddagger}{q_A} e^{-\epsilon_0/kT} \tag{27}$$

In the thermodynamic form (see lecture 5)

$$k_\infty = e^1 \frac{kT}{h} e^{\Delta^\ddagger S^\ominus / R} e^{-E_a / RT} \tag{28}$$

where E_a is the experimentally determined activation energy in the high pressure limit (see lecture course problems).

Conclusions

- The assumption that all modes are harmonic and have the same frequency render the RRK model of little *predictive* use (see Pilling and Seakins p131 for refinements)
- The 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 (RRKM theory)
- Statistical theories don't work when reaction rate becomes competitive with the rate of free energy flow

