

SF Chemical Kinetics.

Lecture 5.

Microscopic theory of chemical reaction kinetics.

Microscopic theories of chemical reaction kinetics.

- A basic aim is to calculate the rate constant for a chemical reaction from first principles using fundamental physics.
- Any microscopic level theory of chemical reaction kinetics must result in the derivation of an expression for the rate constant that is consistent with the empirical Arrhenius equation.
- A microscopic model should furthermore provide a reasonable interpretation of the pre-exponential factor A and the activation energy E_A in the Arrhenius equation.
- We will examine two microscopic models for chemical reactions :
 - The collision theory.
 - The activated complex theory.
- The main emphasis will be on **gas phase bimolecular reactions** since reactions in the gas phase are the most simple reaction types.

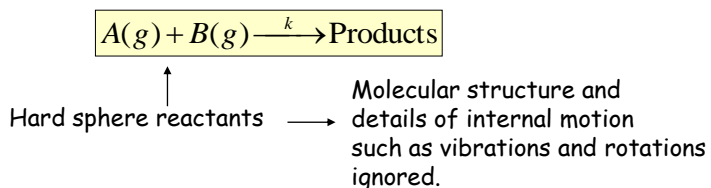
References for Microscopic Theory of Reaction Rates.

- **Effect of temperature on reaction rate.**
 - Burrows et al Chemistry³, Section 8.7, pp.383-389.
- **Collision Theory/ Activated Complex Theory.**
 - Burrows et al Chemistry³, Section 8.8, pp.390-395.
 - Atkins, de Paula, Physical Chemistry 9th edition, Chapter 22, Reaction Dynamics. Section. 22.1, pp.832-838.
 - Atkins, de Paula, Physical Chemistry 9th edition, Chapter 22, Section.22.4-22.5, pp. 843-850.

Collision theory of bimolecular gas phase reactions.

- We focus attention on gas phase reactions and assume that chemical reactivity is due to collisions between molecules.
- The theoretical approach is based on the kinetic theory of gases.
- Molecules are assumed to be hard structureless spheres. Hence the model neglects the discrete chemical structure of an individual molecule. This assumption is unrealistic.
- We also assume that no interaction between molecules until contact.
- Molecular spheres maintain size and shape on collision. Hence the centres cannot come closer than a distance δ given by the sum of the molecular radii.
- The reaction rate will depend on two factors :
 - *the number of collisions per unit time (the collision frequency)*
 - *the fraction of collisions having an energy greater than a certain threshold energy E^* .*

Simple collision theory : quantitative aspects.



Two basic requirements dictate a collision event.

- One must have an A,B encounter over a sufficiently short distance to allow reaction to occur.
- Colliding molecules must have sufficient energy of the correct type to overcome the energy barrier for reaction. A threshold energy E^* is required.

Two basic quantities are evaluated using the Kinetic Theory of gases : the collision frequency and the fraction of collisions that activate molecules for reaction.

To evaluate the collision frequency we need a mathematical way to define whether or not a collision occurs.

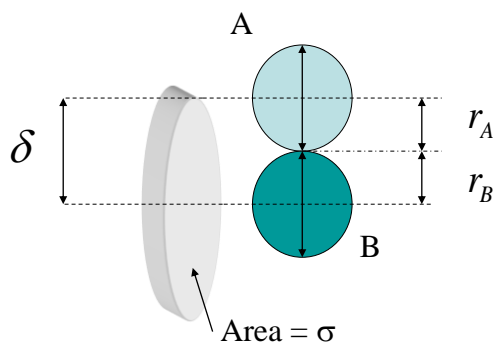
Collision cross section and collision diameter.

The collision cross section σ defines when a collision occurs.

$$\sigma = \pi\delta^2 = \pi(r_A + r_B)^2$$

Effective collision diameter

$$\delta = r_A + r_B$$



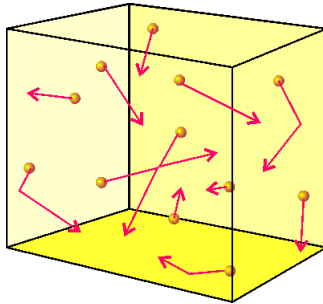
The **collision cross section** for two molecules can be regarded to be the area within which the center of the projectile molecule A must enter around the target molecule B in order for a collision to occur.



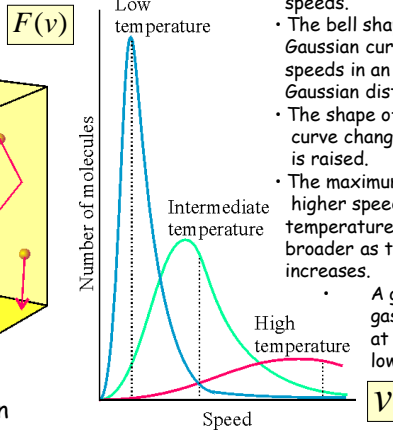
J.C. Maxwell
1831-1879

Maxwell-Boltzmann velocity distribution function

$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2} \exp \left[-\frac{mv^2}{2k_B T} \right]$$



Gas molecules exhibit a spread or distribution of speeds.



- The velocity distribution curve has a very characteristic shape.
- A small fraction of molecules move with very low speeds, a small fraction move with very high speeds, and the vast majority of molecules move at intermediate speeds.
- The bell shaped curve is called a Gaussian curve and the molecular speeds in an ideal gas sample are Gaussian distributed.
- The shape of the Gaussian distribution curve changes as the temperature is raised.
- The maximum of the curve shifts to higher speeds with increasing temperature, and the curve becomes broader as the temperature increases.
- A greater proportion of the gas molecules have high speeds at high temperature than at low temperature.

The collision frequency is computed via the kinetic theory of gases.

We define a collision number (units: $m^{-3}s^{-1}$) Z_{AB} .

$$Z_{AB} = \pi \delta^2 n_A n_B \langle v_r \rangle$$

← Mean relative velocity
Units: m^2s^{-1}

n_j = number density of molecule j (units : m^{-3}) $\delta = r_A + r_B$

Mean relative velocity evaluated via kinetic theory.

Average velocity of a gas molecule

$$\langle v \rangle = \int_0^\infty v F(v) dv$$

$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2} \exp \left[-\frac{mv^2}{2k_B T} \right]$$

Maxwell-Boltzmann Distribution function

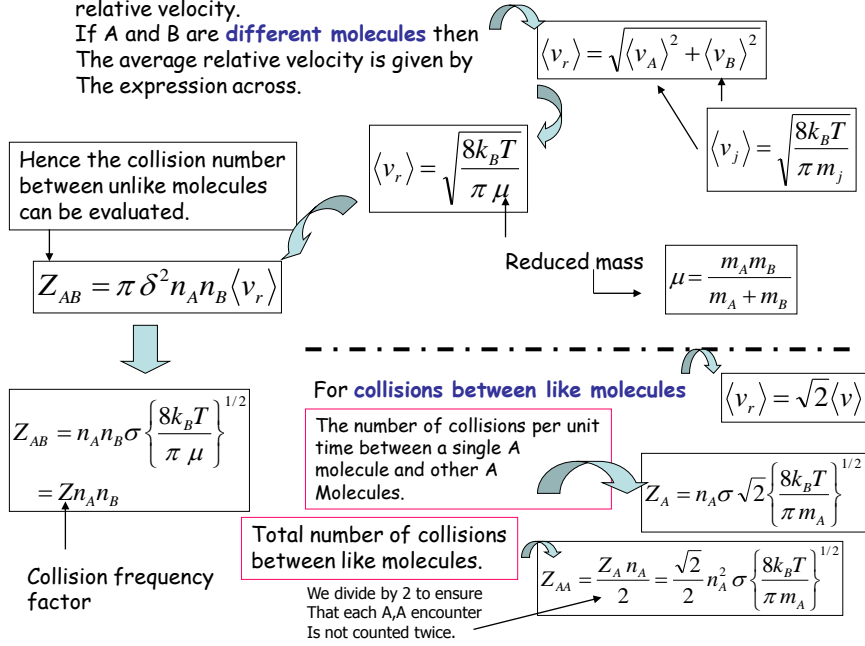
MB distribution of velocities enables us to statistically estimate the spread of molecular velocities in a gas

Some maths !

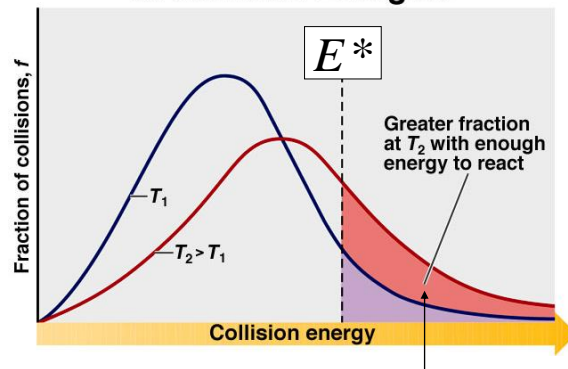
$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

← Mass of molecule

We now relate the average velocity to the mean relative velocity.
 If A and B are **different molecules** then the average relative velocity is given by the expression across.



Temperature and the Distribution of Collision Energies



Molecular collision is effective only if translational energy of reactants is greater than some threshold value.

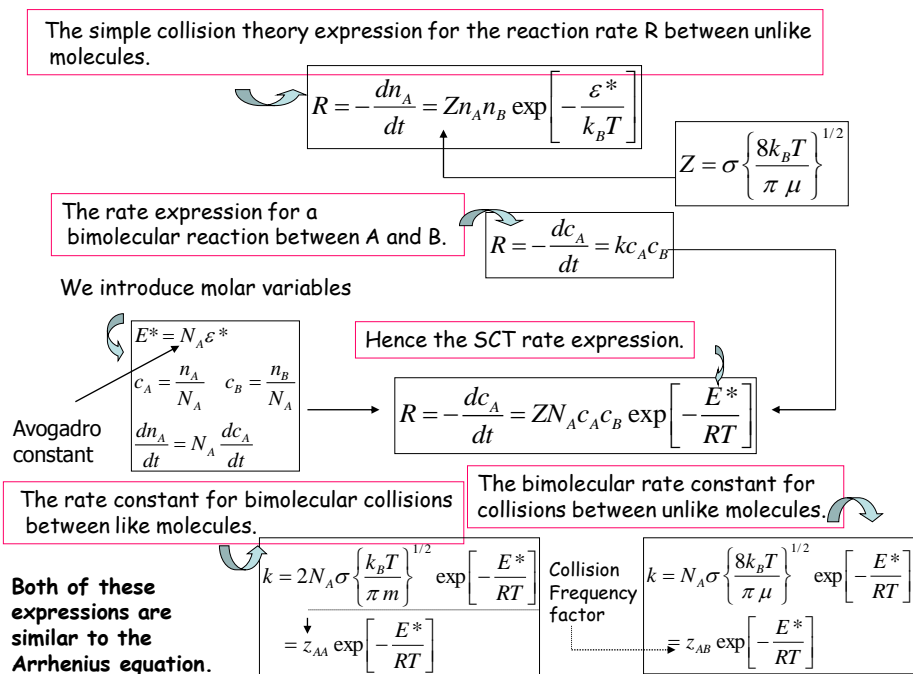
Fraction of molecules with kinetic energy greater than some minimum threshold value ϵ^*

$$F(\epsilon > \epsilon^*) = \exp \left[-\frac{\epsilon^*}{k_B T} \right]$$

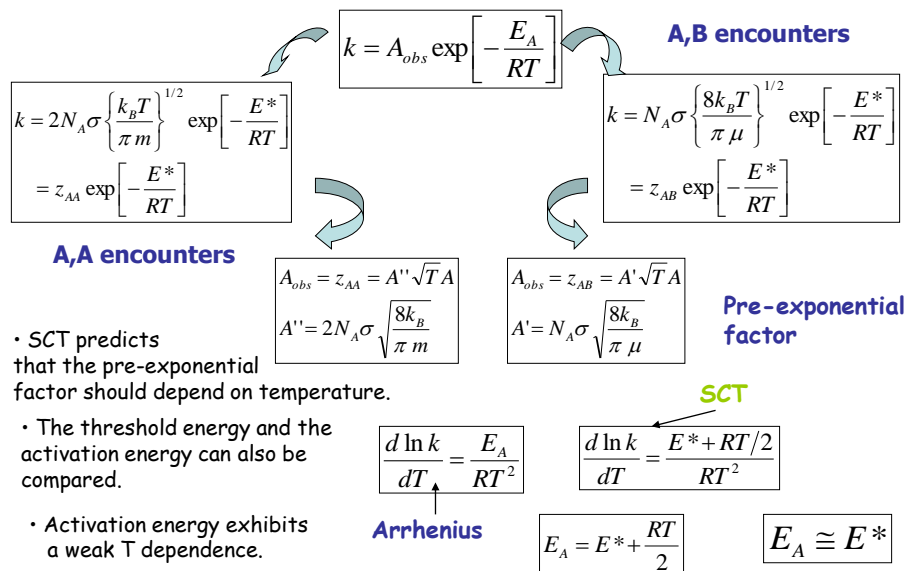
Activation Energy

Table 16.5 The Effect of E_a and T on the Fraction (f) of Collisions with Sufficient Energy to Allow Reaction

E_a (kJ/mol)	f (at $T = 298$ K)
50	1.70×10^{-9}
75	7.03×10^{-14}
100	2.90×10^{-18}
T	f (at $E_a = 50$ kJ/mol)
25°C (298 K)	1.70×10^{-9}
35°C (308 K)	3.29×10^{-9}
45°C (318 K)	6.12×10^{-9}



We compare the results of SCT with the empirical Arrhenius eqn. in order to obtain an interpretation of the activation energy and pre-exponential factor.



SCT : a summary.

- The major problem with SCT is that the threshold energy E^* is very difficult to evaluate from first principles.
- The predictions of the collision theory can be critically evaluated by comparing the experimental pre-exponential factor with that computed using SCT.
- We define the **steric factor** P as the ratio between the experimental and calculated A factors.
- We can incorporate P into the SCT expression for the rate constant.
- For many gas phase reactions P is considerably less than unity.
- Typically SCT will predict that A_{calc} will be in the region 10^{10} - 10^{11} $\text{L mol}^{-1} \text{s}^{-1}$ regardless of the chemical nature of the reactants and products.
- What has gone wrong? The SCT assumption of hard sphere collision neglects the important fact that **molecules possess an internal structure**. It also neglects the fact that the relative orientation of the colliding molecules will be important in determining whether a collision will lead to reaction.
- We need a better theory that takes molecular structure into account. The **activated complex theory** does just that.

$$P = A_{exp} / A_{calc}$$

$$k = P z_{AB} \exp \left[-\frac{E^*}{RT} \right]$$

$$k = P z_{AA} \exp \left[-\frac{E^*}{RT} \right]$$

Summary of SCT.

A, B encounters

$$k = N_A \sigma \left\{ \frac{8k_B T}{\pi \mu} \right\}^{1/2} \exp \left[-\frac{E^*}{RT} \right]$$

$$= z_{AB} \exp \left[-\frac{E^*}{RT} \right]$$

A, A encounters

$$k = 2N_A \sigma \left\{ \frac{k_B T}{\pi m} \right\}^{1/2} \exp \left[-\frac{E^*}{RT} \right]$$

$$= z_{AA} \exp \left[-\frac{E^*}{RT} \right]$$

Transport property Energy criterion

$$k = P z_{AB} \exp \left[-\frac{E^*}{RT} \right]$$

$$k = P z_{AA} \exp \left[-\frac{E^*}{RT} \right]$$

Steric factor
(Orientation requirement)

Weaknesses:

- No way to compute P from molecular parameters
- No way to compute E* from first principles. Theory not quantitative or predictive.

Strengths:

- Qualitatively consistent with observation (Arrhenius equation).
- Provides plausible connection between microscopic molecular properties and macroscopic reaction rates.
- Provides useful guide to upper limits for rate constant k.



Henry Eyring
1901-1981

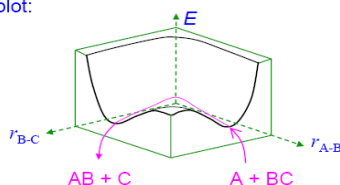
Developed (in 1935) the Transition State Theory (TST) or Activated Complex Theory (ACT) of Chemical Kinetics.

Potential Energy Surfaces 1

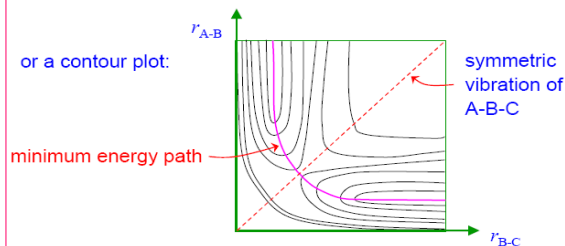
A **reaction surface** is a plot of the energy of a reaction system as a function of all the independent variables (bond lengths and bond angles). Even a collinear triatomic reaction such as



needs a 3-D plot:

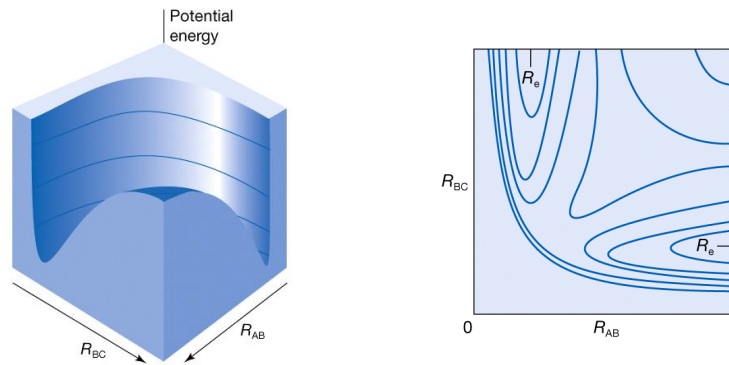


or a contour plot:

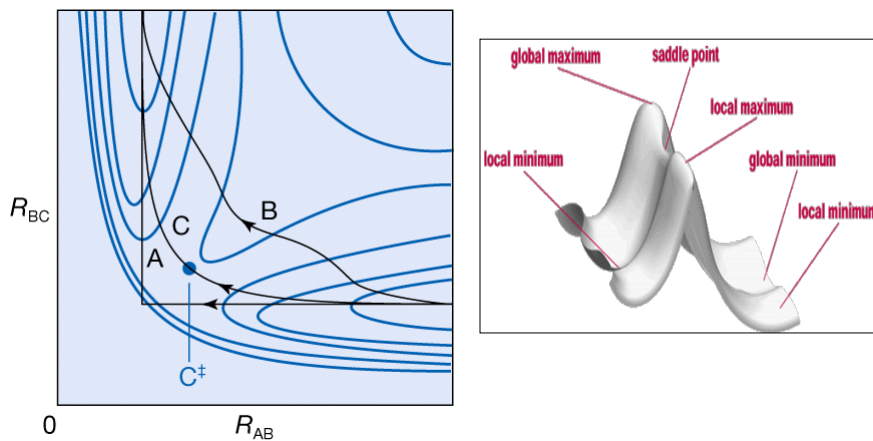


Potential energy surface

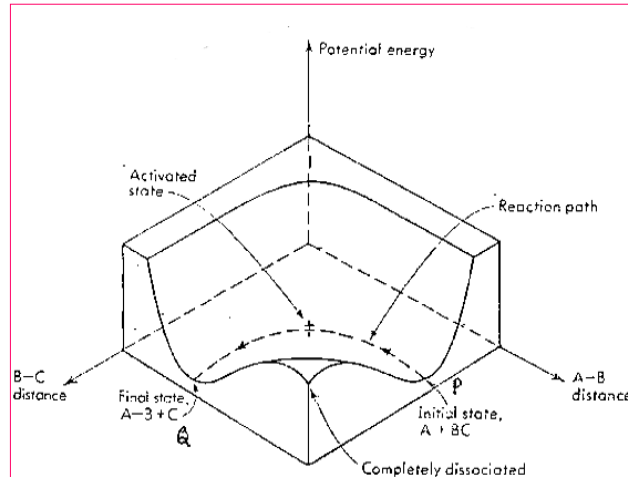
- Can be constructed from experimental measurements or from Molecular Orbital calculations, semi-empirical methods,.....



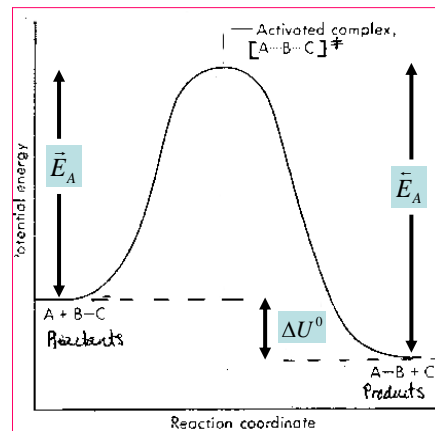
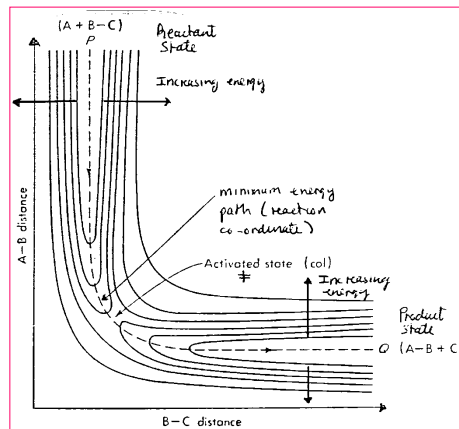
Various trajectories through the potential energy surface



Potential energy hypersurface for chemical reaction between atom and diatomic molecule.

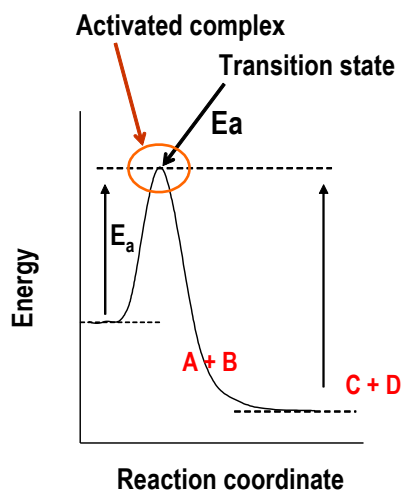


Reading reaction progress on PE hypersurface.



Transition state theory (TST) or activated complex theory (ACT).

- In a reaction step as the reactant molecules **A** and **B** come together they distort and begin to share, exchange or discard atoms.
- They form a loose structure AB^\ddagger of high potential energy called the **activated complex** that is poised to pass on to products or collapse back to reactants **C + D**.
- The peak energy occurs at the **transition state**. The energy difference from the ground state is the **activation energy** E_a of the reaction step.
- The potential energy falls as the atoms rearrange in the cluster and finally reaches the value for the products
- Note that the reverse reaction step also has an activation energy, in this case higher than for the forward step.

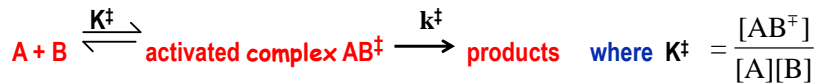


Transition state theory

- The theory attempts to explain the size of the rate constant k_r and its temperature dependence from the actual progress of the reaction (**reaction coordinate**).
- The progress along the **reaction coordinate** can be considered in terms of the approach and then reaction of an **H** atom to an **F₂** molecule
- When far apart the potential energy is the sum of the values for **H** and **F₂**
- When close enough their orbitals start to overlap
 - A bond starts to form between **H** and the closer **F** atom $H \cdots F-F$
 - The **F-F** bond starts to lengthen
- As **H** becomes closer still the $H \cdots F$ bond becomes shorter and stronger and the **F-F** bond becomes longer and weaker
 - The atoms enter the region of the activated complex
- When the three atoms reach the point of maximum potential energy (the transition state) a further infinitesimal compression of the **H-F** bond and stretch of the **F-F** bond takes the complex through the transition state.

Thermodynamic approach

- Suppose that the activated complex AB^\ddagger is in equilibrium with the reactants with an equilibrium constant designated K^\ddagger and decomposes to products with rate constant k^\ddagger



- Therefore rate of formation of products = $k^\ddagger [AB^\ddagger] = k^\ddagger K^\ddagger [A][B]$
- Compare this expression to the rate law: rate of formation of products = $k_r [A][B]$
- Hence the rate constant $k_r = k^\ddagger K^\ddagger$
- The Gibbs energy for the process is given by $\Delta^\ddagger G = -RT \ln(K^\ddagger)$ and so $K^\ddagger = \exp(-\Delta^\ddagger G/RT)$
- Hence rate constant $k_r = k^\ddagger \exp(-(\Delta^\ddagger H - T\Delta^\ddagger S)/RT)$.
- Hence $k_r = k^\ddagger \exp(\Delta^\ddagger S/R) \exp(-\Delta^\ddagger H/RT)$
- This expression has the same form as the Arrhenius expression.
 - The activation energy E_a relates to $\Delta^\ddagger H$
 - Pre-exponential factor $A = k^\ddagger \exp(\Delta^\ddagger S/R)$
 - The steric factor P can be related to the change in disorder at the transition state

Statistical thermodynamic approach

- The activated complex can form products if it passes through the transition state AB^\ddagger
- The equilibrium constant K^\ddagger can be derived from statistical mechanics

$$K^\ddagger = \frac{q_{AB^\ddagger}}{q_A q_B} \exp\left(-\frac{\Delta E_0}{RT}\right)$$

 - q is the partition function for each species
 - ΔE_0 (kJ mol⁻¹) is the difference in internal energy between A , B and AB^\ddagger at $T=0$
- Suppose that a very loose vibration-like motion of the activated complex AB^\ddagger with frequency ν along the reaction coordinate tips it through the transition state.
 - The reaction rate depends on the frequency of that motion. Rate = $\nu [AB^\ddagger]$
- It can be shown that the rate constant k_r is given by the Eyring equation

$$k_r = \frac{kT}{h} K^\ddagger$$

$$\text{Hence } k_r = \frac{kT}{h} \frac{q_{AB^\ddagger}}{q_A q_B} \exp\left(-\frac{\Delta E_0}{RT}\right)$$

 - the contribution from the critical vibrational motion has been resolved out from quantities K^\ddagger and q_{AB^\ddagger}
 - ν cancels out from the equation
 - k = Boltzmann constant h = Planck's constant

Statistical thermodynamic approach

- Can determine partition functions q_A and q_B from spectroscopic measurements but transition state has only a transient existence (picoseconds) and so cannot be studied by normal techniques (into the area of femtochemistry)
- Need to postulate a structure for the activated complex and determine a theoretical value for q^\ddagger .
 - Complete calculations are only possible for simple cases, e.g., $H + H_2 \rightarrow H_2 + H$
 - In more complex cases may use mixture of calculated and experimental parameters
- Potential energy surface: 3-D plot of the energy of all possible arrangements of the atoms in an activated complex. Defines the easiest route (the col between regions of high energy) and hence the exact position of the transition state.
- For the simplest case of the reaction of two structureless particles (e.g., atoms) with no vibrational energy reacting to form a simple diatomic cluster the expression for k_r derived from statistical thermodynamics resembles that derived from collision theory.
 - Collision theory works.....for 'spherical' molecules with no structure

Example of a potential energy surface

- Hydrogen atom exchange reaction
 $H_A + H_B-H_C \rightarrow H_A-H_B + H_C$
- Atoms constrained to be in a straight line (collinear) $H_A \cdots H_B \cdots H_C$
- Path C goes up along the valley and over the col (pass or saddle point) between 2 regions (mountains) of higher energy and descends down along the other valley.
- Paths A and B go over much more difficult routes through regions of high energy
- Can investigate this type of reaction by collision of molecular/ atomic beams with defined energy state.
 - Determine which energy states (translational and vibrational) lead to the most rapid reaction.

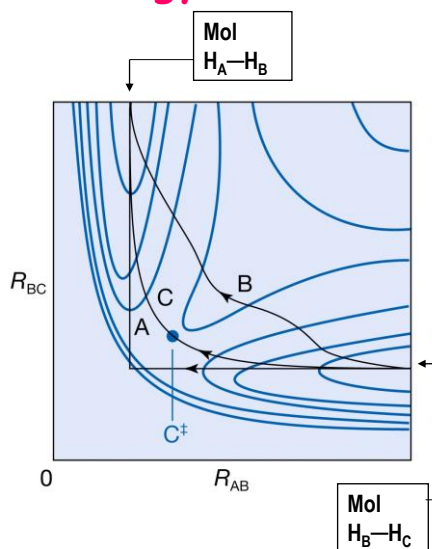


Diagram: www.oup.co.uk/powerpoint/bt/atkins

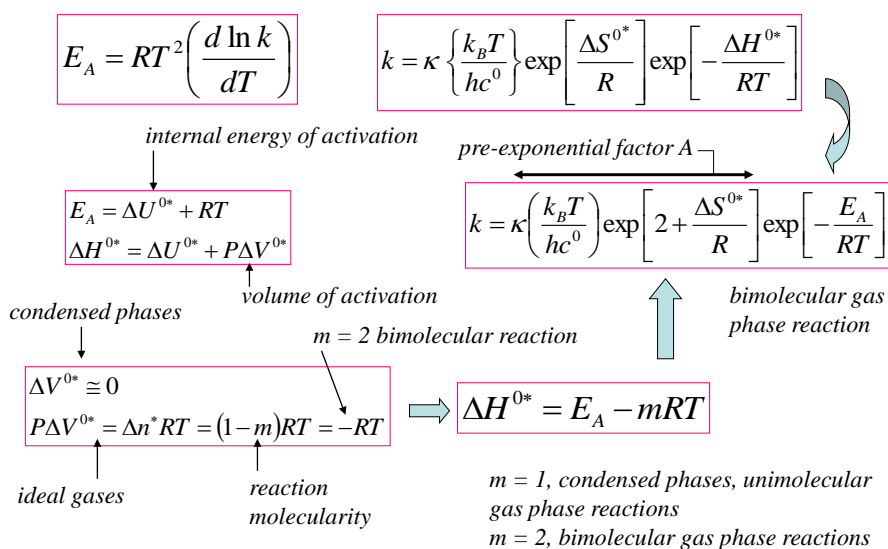
Advantages of transition state theory

- Provides a complete description of the nature of the reaction including
 - the changes in structure and the distribution of energy through the transition state
 - the origin of the pre-exponential factor A with units t^{-1} that derive from frequency or velocity
 - the meaning of the activation energy E_a
- Rather complex fundamental theory can be expressed in an **easily understood pictorial diagram of the transition state** - plot of energy vs the reaction coordinate
- The pre-exponential factor A can be derived *a priori* from statistical mechanics in simple cases
- The steric factor P can be understood as related to the change in order of the system and hence the entropy change at the transition state
- Can be applied to reactions in gases or liquids
- Allows for the influence of other properties of the system on the transition state (e.g., **solvent effects**).

Disadvantage

- Not easy to estimate fundamental properties of the transition state except for very simple reactions
 - theoretical estimates of A and E_a may be 'in the right ball-park' but still need experimental values

Relating ACT parameters and Arrhenius Parameters.



ACT interpretation of Arrhenius Equation.

$$k_m = \kappa \left(\frac{k_B T}{h(c^0)^{m-1}} \right) \exp \left[m + \frac{\Delta S^{0*}}{R} \right] \exp \left[-\frac{E_A}{RT} \right]$$

$m = \text{molecularity}$

ΔS^{0*} explained in terms of changes in translational, rotational and vibrational degrees of freedom on going from reactants to TS.

$$A = \kappa \left(\frac{k_B T}{h(c^0)^{m-1}} \right) \exp \left[m + \frac{\Delta S^{0*}}{R} \right]$$

Pre-exponential factor related to entropy of activation (difference in entropy between reactants and activated complex)

$$A = PZ = \kappa \left(\frac{k_B T}{h(c^0)^{m-1}} \right) \exp \left[m + \frac{\Delta S^{0*}}{R} \right]$$

collision theory

steric factor

$$P \cong 1 \quad \Delta S^{0*} \cong 0$$

$$P < 1 \quad \Delta S^{0*} \text{ negative}$$

$$P > 1 \quad \Delta S^{0*} \text{ positive}$$

TS more ordered than reactants

TS less ordered than reactants

