Lecture 14
Theories of Reaction Rates

There are two basic theories: Collision theory and activated complex theory.

Simplest is the collision theory – accounts for gas phase reactions

Reactions in solution
   1. Diffusion controlled - Diffusion equation can account for rates
   2. Activation controlled – Activated complex and thermodynamics are involved

Rates in terms of potential energy surfaces is the more advanced

Both (collision and activated complex) theories say that:
Molecular encounters make them excited making reactions. Excitation can be through collisions (collision theory) or the energy can be taken from surroundings (activated complex, in solutions).

Collision Theory

A + B $\rightarrow$ Products

Rate = k_2[A][B]

k_2 to involve 1. Energy 2. Orientation 3. Rate of encounter

k_2 α rate of collisions x steric requirement x energy requirement

Assumptions

- Molecules are hard spheres
- For reactions to occur, molecules must collide
- Reactions occur only if molecules are energetic
- Collisions should transfer certain minimum energy

Number of Collisions

Number of molecules N in volume V

Number of collisions of one molecule per second

is the collision frequency, z

Average velocity of the molecule = $\bar{V}$ m/s, the molecule collides every molecule within the distance, d

Therefore, all the molecules within the volume $\pi d^2 \bar{V}$ will collide with the test molecule per second.

πd^2
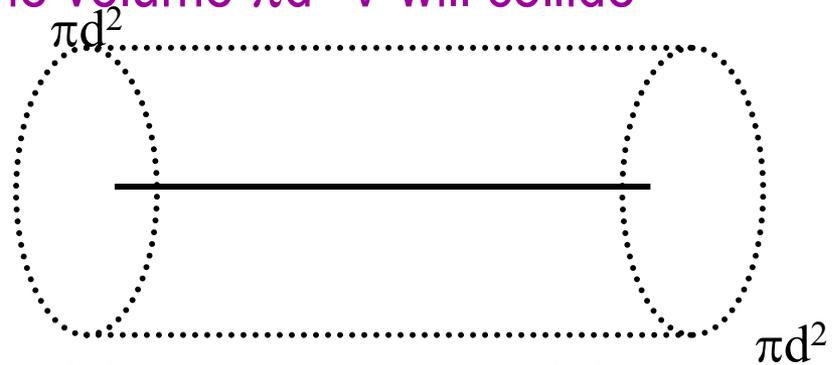
Encounter of A with B

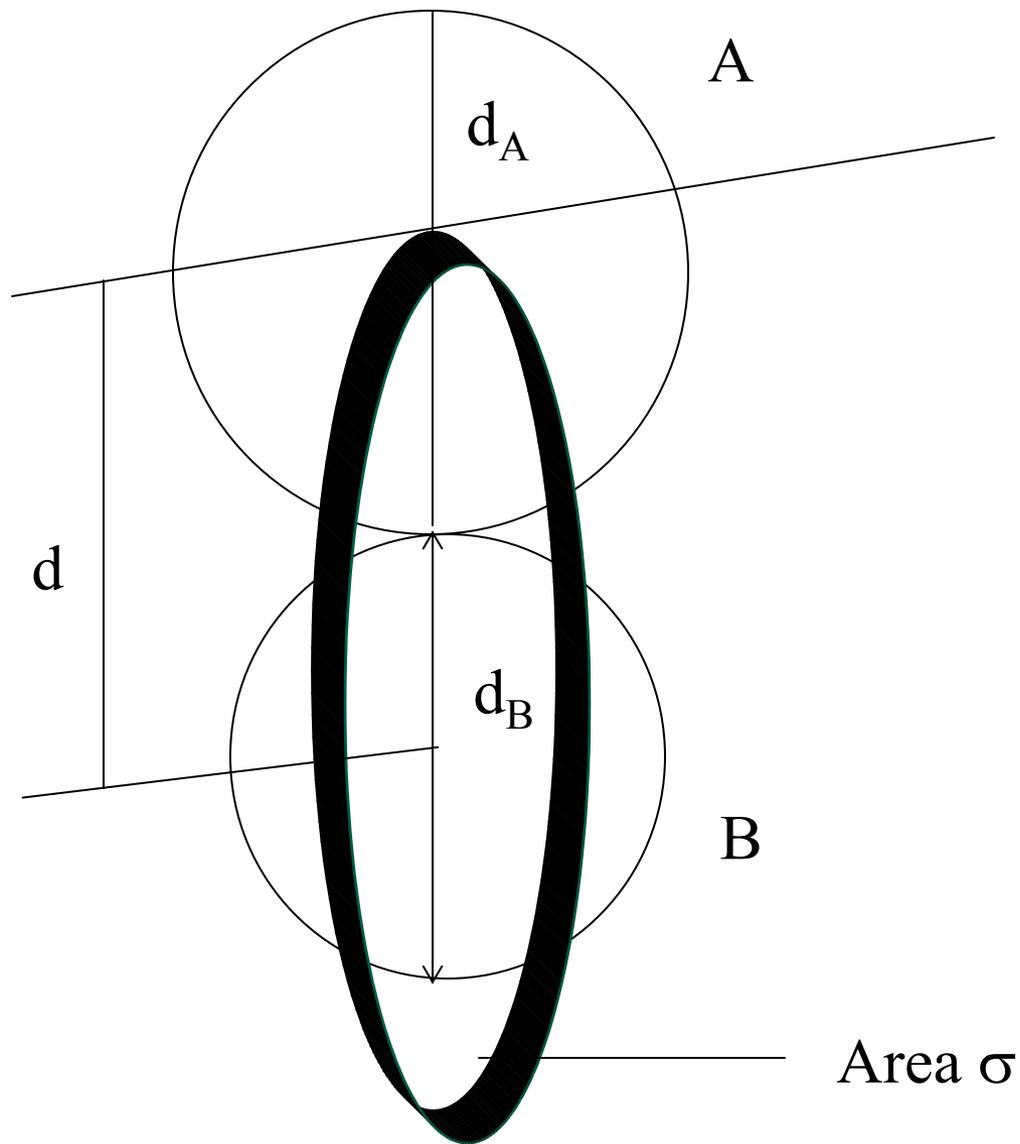πd^2 - collision cross section

This is the area within which centre of A has to enter around the target molecule B for collisions to occur.

πd^2

This is the Volume swept by the molecule/sec

The solid line represents the average velocity of the molecule.

Area πd^2, is the area covered by the dotted lines.

A

d_A

d

d_B

B

Area σ

N/V $\rightarrow$ Number of molecules in unit volume

Number of collisions of one molecule per second,

$z = (N/V) (\pi d^2) (\overline{V} \text{ s}^{-1})$

Average speed $\overline{V} = (8kT/\pi m)^{½}$

m is replaced by $\mu = (m_1 m_2/m_1 + m_2)$, reduced mass

identical particles $\mu = m/2$

$\overline{V} = (8kT/\pi m/2)^{½}$

$z_{11} = \sqrt{2} \text{ N/V } \pi d^2 (8kT/\pi m)^{½} \text{ s}^{-1}$

$z_{11} = \sqrt{2} \text{ N/V } \pi d^2 (8RT/\pi M)^{½} \text{ s}^{-1}$

$\pi d^2 = \sigma \leftarrow$ Collision cross – section

$z_{11} = \sqrt{2} \text{ N/V } \sigma (8kT/\pi m)^{½} \text{ s}^{-1}$

Collision number

Number of bimolecular collisions in 1 m^3 per sec,

Z_{11} ($s^{-1}m^{-3}$) = ½ N/V z_{11}

½ not to count collisions twice

$= 1/\sqrt{2}$ $(N/V)^2$ πd^2 $\bar{V}$

for different molecules,

$Z_{12} = (N_A/V)(N_B/V) \pi (r_1 + r_2)^2 (8kT/\pi \mu)^{\frac{1}{2}}$

Collision Number is very large ~ 10^{34} for N_2 at STP

Rate constant

A + B $\rightarrow$ P

d[P]/dt = k[A][B]

if all collisions lead to reactions,

d[P]/dt = Z_{AB}/Nav

Nav $\rightarrow$ Avogadro number

(Since rate is in moles/unit volume and not in molecules/unit volume)

We know,

d[P]/dt = k (N_A/V.Nav) (N_B/V.Nav) ... 1

d[P]/dt = Z_{AB}/Nav = 1/Nav (N_A/V) (N_B/V) $\pi d^2 \bar{V}$ ... 2

Compare 1 and 2

k/Nav = $\pi d^2 \bar{V}$

k = Nav$\pi d^2 \bar{V}$ mol^{-1}m^{3}s^{-1}

k = Navσ (8kT/$\pi \mu$)^{½} m^3 mol^{-1} s^{-1}

The actual value is very very small !! H_2 + I_2 $\rightarrow$ HI, Calculated

k = 7.5 x 10^8 m^3 mol^{-1} s^{-1} = 7.5 x 10^{11} L mol^{-1} s^{-1}

Observed $\rightarrow$ 1.15 x 10^{-4} L mol^{-1} s^{-1} !!!

Energy Considerations

We expect the rate constant for a bimolecular reaction to depend on both frequency and energy of the collisions.

The above considerations do not take into account the role of energy:

The reaction of molecular pairs with energy above Ea is given by

$= \exp.^{-Ea/RT}$

These are the fruitful collisions leading to products.

Z_{AB} (effective) $= Z_{AB} \times \exp^{-Ea/RT}$

The rate constant for a bimolecular reactions is

$k' = N_{AV} \pi d^2_{AB} (8kT/\pi m_r)^{\frac{1}{2}} \exp^{-Ea/RT}$

This equation is similar to the Arrhenius law except for $\sqrt{T}$ term in $\overline{V}_{AB}$ of pre-experimental factor.

Kinetic data over a wide range of temperature range show that the pre-experimental factor depends on $\sqrt{T}$ (by about 2%) as predicted.

$\therefore k = A'\sqrt{T} \exp^{-Ea/RT}$

$A' = N_{AV} \pi d^2_{AB} (8k/\pi m_r)^{\frac{1}{2}} \, mol^{-1} \, m^3 \, sec^{-1}$

Steric requirement

Collision energy is not the only criterion.

Relative orientation is important.

Disagreement in A values between theory and experiment

Explained in terms of a steric factor, P

$k_{11} = P\ Z_{11}\ e^{-Ea/RT}$

$k_{12} = P\ Z_{12}\ e^{-Ea/RT}$

$P = (A_{expt}/A_{theory})$

Different equations used

For like molecules

Rate = Z_{AA}/N_{AV} = $1/\sqrt{2}$ $(N_A/V)^2 \pi d^2$ $\overline{V}$ $(1/N_{AV})$

Rate = k $(N_A/V\ N_{AV})$ $(N_A/\ V\ N_{AV})$ = $1/\sqrt{2}$ $(N_A/V)^2 \sigma$ $\overline{V}$ $(1/N_{AV})$

k/N_{AV} = $1/\sqrt{2}$ πd^2 $\overline{V}$

k = $1/\sqrt{2}$ N_{AV} πd^2 $\overline{V}$

= $1/\sqrt{2}$ N_{AV} πd^2 $(8kT/\pi m)^{1/2}$

= 2 N_{AV} d^2 $(\pi kT/m)$ mol^{-1} m^3 s^{-1}

k = 2 N_{AV} d^2 $(\pi RT/M)^{1/2}$ $e^{-Ea/RT}$

The steric factor is difficult to evaluate

$$k = P\sigma(8kT/\pi\mu)^{1/2} N_A e^{-Ea/RT}$$

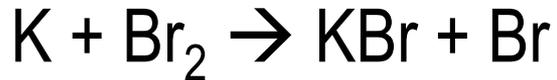The effective σ can be considered as $P\sigma$ which is taken as the reactive cross section σ^*.

$$k = P\sigma(8kT/\pi\mu)^{1/2} N_A e^{-Ea/RT}$$
$$k = A e^{-Ea/RT}$$
$$A = P\sigma(8kT/\pi\mu)^{1/2} N_A$$

This kind of evaluation shows that P is very small, of the order of 10^{-6}

One case where P is large is for the reaction,

K + Br$_2$ $\rightarrow$ KBr + Br

Here P = 4.8 (experimentally)

Suggested to follow Harpoon Mechanism

Harpoon extends the cross-section of reactive encounter

Reaction need not occur as a result of simple mechanical encounter

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Calculate P assuming harpoon mechanism

Net change in energy upon transfer of an electron from K to Br$_2$

to form K$^+$ and Br$_2^-$ is

E= I – E$_a$ - e^2/(4 πε$_o$R), this will go to zero when harpoon will transfer

e^2/4πε$_o$R = I – E$_a$

So, P = σ*/σ = R^2/d^2 = {e^2/4 πε$_o$ (I-E$_a$)}^{2} d^2

Value determined is 4.2, in agreement with experiment (4.8).

Transition State Theory

Other names: Activated complex theory and Absolute rate theory

Drawbacks of collision theory:

Difficult to calculate the steric factor from molecular geometry for complex molecules.
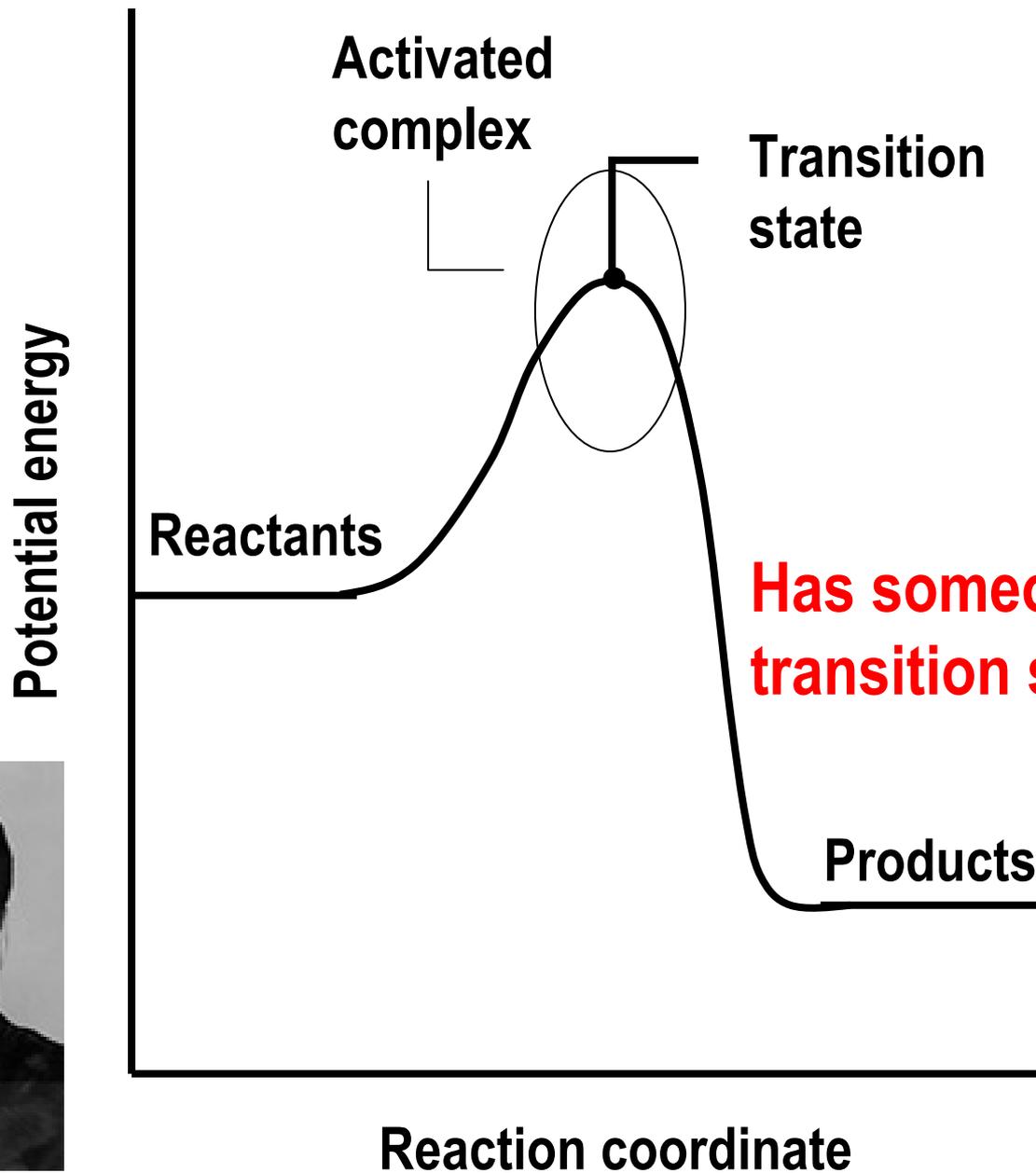
The theory is applicable essentially to gaseous reactions

Consider A + B $\rightarrow$ P or A + BC = AB + C

$$A + B = [AB]^{\ddagger} \xrightarrow{k_2} P$$

A and B form an activated complex and are in equilibrium with it.

The reactions proceed through an activated or transition state which has energy higher than the reactions or the products.

The rate depends on two factors,

(i). Concentration of [AB]

(ii). The rate at which activated complex is decomposed.

∴ Rate of reaction = [AB‡] x frequency of decomposition of AB‡

$K^{\ddagger}_{eq}$ = [AB‡] / [A] [B]

[AB‡] = $K^{\ddagger}_{eq}$ [A] [B]

The activated complex is an aggregate of atoms and assumed to be an ordinary molecule. It breaks up into products on a special vibration, along which it is unstable.

The frequency of such a vibration is equal to the rate at which activated complex decompose.

-d[A]/dt = -d[B]/dt = k_2[A][B]

Rate of reaction = [AB‡] υ

$\qquad\qquad\quad$ = $K^{\ddagger}_{eq}$ υ [A] [B]

Activated complex is an unstable species and is held together by loose bonds.

$\therefore$ The vibration of low frequency will decompose the activated complex.

$\therefore$ Energy of vibration $E = h\upsilon$

$\upsilon = E/h = k_BT/h$

In a classical sense, the average energy of such a vibrational degree of freedom, k_BT (where $k_B = R/N$). Remember equipartition principle.

If we know the energy distribution of molecules clearly (statistical mechanics) we can make a better description.

$k = k_B T/h \, K^{\ddagger}_{eq} \, (C^o)^{1-m}$ **Eyring equation**

C° is the standard – state concentration of 1 mol L^{-1}, m is the order.
The factor $(C^{\circ})^{1-m}$ is introduced because equilibrium constant is
dimensionless, but the units for rate constant depend on the order
of the reaction.

$\therefore k = k_B \, (J \, K^{-1}) \, T \, (K)/h \, (J \, s) \quad K^{\ddagger} \quad (C^{\circ})^{(1-m)}$

$\uparrow$

Dimensionless

k is in s^{-1} for 1st order
for second order, $L \, mol^{-1}s^{-1} = s^{-1}(C^{\circ})^{-1}$

$\therefore k_2 = K^{\ddagger}_{eq} \, k_B T/h$

$K^{\ddagger}$ for the formation of the transition state can be written in terms
of the molecular partition functions for the reactants and the
transition state.

Thermodynamic Aspects

The equilibrium constant $K^{\ddagger}_{eq}$ can be interpreted in terms of $\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$.

These quantities represent the difference between the values of the respective thermodynamic functions between activated complex and reactants.

All substances being in their standard states, is activity of unity.

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

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

$\Delta H^{\ddagger} - T\Delta S^{\ddagger} = -RT \ln K^{\ddagger}_{eq}$

$K^{\ddagger}_{eq} = \exp(-\Delta H^{\ddagger}/RT) \exp \Delta S^{\ddagger}/R$

In the form of Arrhenius Equation $\rightarrow \therefore k_2 = k_B T/h \; \exp^{-\Delta H^{\ddagger}/RT} \exp^{\Delta S^{\ddagger}/R}$

This can be expressed in a form which involves E_a (experimental) instead of $\Delta H^{\ddagger}$.

We need to find relation between $\Delta H^{\ddagger}$ and E_a.

The variation of $K_{eq}^{\ddagger}$ with temperature is given by,

$d(\ln K_{eq}^{\ddagger})/dT = \Delta E^{\ddagger}/RT^2$ (one form of Arrhenius law).

The assumption here is that K is actually, K_c.

$\Delta E^{\ddagger}$ represents the increase in energy when reactants go from the initial state to the activated state.

$k_2 = K_{eq}^{\ddagger} k_B T/h$

$\ln k_2 = \ln T + \ln K_{eq}^{\ddagger} + \ln k_B/h$

Differentiate with respect to temperature and rewrite.

$d \ln k_2/dT = 1/T + d\ln K_{eq}^{\ddagger}/dT$

$\therefore d \ln k_2/dT = 1/T + \Delta E^{\ddagger}/RT^2$

$\therefore d \ln k_2/dT = (RT + \Delta E^{\ddagger})/RT^2$

Compare this with Arrhenius equation

$d \ln k/dT = E_a/RT^2$

We get $E_a = \Delta E^{\ddagger} + RT$

$[\Delta E^{\ddagger} \equiv \Delta U^{\ddagger}]$ $H = E + PV$

Or $E_a = \Delta H^{\ddagger} - P\Delta V^{\ddagger} + RT$

$\Delta E^{\ddagger} = \Delta H^{\ddagger} - P\Delta V^{\ddagger}$ or $\Delta U^{\ddagger} = \Delta H^{\ddagger} - P\Delta V^{\ddagger}$ at constant p

$P\Delta V^{\ddagger} = \Delta n^{\ddagger} RT$

For ideal gases, it becomes

$E_a = \Delta H^{\ddagger} + RT - \Delta n^{\ddagger} RT$

$\Delta V^{\ddagger}$ is volume change and $\Delta n^{\ddagger}$ is the change in number of moles from initial state to the activated state.

For bimolecular reaction

$\Delta n^{\ddagger} = -1$

$E_a = \Delta H^{\ddagger} + RT - (-1)RT$

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

$\therefore \; k_2 = k_B T/h \; \exp^{\Delta S^{\ddagger}/R} \; \exp^{-(Ea- 2RT)/RT}$

$k_2 = k_B T/h \; e^2 \; \exp^{\Delta S^{\ddagger}/R} \; \exp^{-Ea/RT}$

Note this e^2

$\Delta S^{\ddagger}$ can be calculated form k_2 & E_a.

This terms is the A in the Arrhenius expression

Can we show that A is the same by both the theories?

For reactions in solution and for unimolecular reactions, $\Delta H^{\ddagger} \approx E_a$ (almost equal)

$\Delta S^{\ddagger}$ negative means activated complex is more ordered than the reactants and A will have smaller value

$A = k_B T/h \, \exp^{\Delta S^{\ddagger}/R} \, e$ (unimolecular)
$A = k_B T/h \, \exp^{\Delta S^{\ddagger}/R} \, e^2$ (bimolecular)

And reaction will be slower.

Positive $\Delta S^{\ddagger}$ means that entropy of the complex is greater than the entropy of the reactants.

A loosely bound complex has a higher entropy of activation than a tightly bound one.

Multiply rate constants with a factor $(C^{\circ})^{1-m}$ to take care of the units of the rate constants (which depend on order).

Example: For the reaction
$CH_3 + D_2 \rightarrow CH_3D + D$, the rate constant is given by
$k = 2 \times 10^9 \exp^{-6389/T}$ $M^{-1}s^{-1}$ over the temperature range 300 to 626 K
calculate enthalpy and entropy of activation for this reactions at 300K.
Since n = -1.
$\Delta H^{\ddagger} = E_a - 2RT$
= 6389 x 8.314 – 2 x 8.314 x 300
= 48.1 kJ/mol
$\exp \Delta S^{\ddagger}/R = AhC_o/k_B Te^2$
= $((2 \times 10^9 M^{-1}s^{-1}) (6.63 \times 10^{-34} \text{ Js}) (1M))/(1.38 \times 10^{-23} JK^{-1}) (300K) e^2))$
= 4.35×10^{-15}
$\therefore \Delta S^{\ddagger} = -83.50 \text{ } JK^{-1} mol^{-1}$
ΔS is negative; which means that the activated complex is more restricted than the reactants. This suggests the formation of a complex between CH_3 and D_2 with a bond energy ~48 kJ. Evidently, the structure of the complex is rigid enough (vibrational frequencies are high).

Dynamics of molecular collisions

Reactions between species are better understood by undertaking studies in the gas phase. Here molecular beams can be used to study reactive collisions. Reactants can be prepared in selected energy states and the products can be studied as a function of their energy states. In the case of a typical kinetics experiment, there is a distribution of energy states. The study of factors governing collisions of molecules constitute the area called reaction dynamics. The results can be better understood in terms of potential energy surfaces. For example, the collision to a hydrogen molecule (H_2) and a hydrogen atom (H) can be represented in terms of a potential energy surface. In this system, it is known that the lowest energy of interaction is when the collision is along a line. The variation in the potential energy of the system as a function of two distances give the potential energy surface. This is depicted below. The interaction can also be depicted in terms of a contour diagram. There are also other approaches. A study of this collision tells how the molecule H_A-H_B results in the formation of H_B-H_C upon collision with an H atom and the various factors which govern this reactive encounter. Such a procedure can be extended to more complicated systems.

Potential energy

R_{BC}

R_{AB}