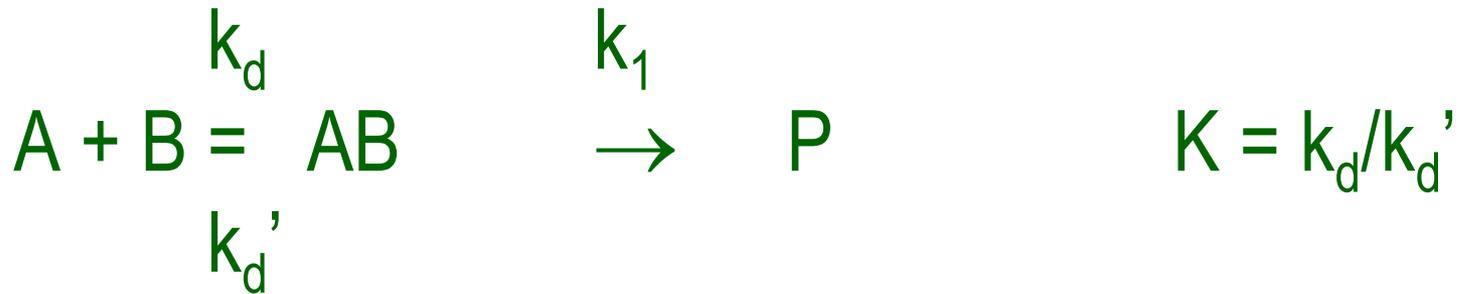


Lecture 17

Transition State Theory

Reactions in solution



$$d[AB]/dt = k_d[A][B] - k_d'[AB] - k_1[AB]$$

$$[AB] = k_d[A][B]/k_1 + k_d'$$

$$d[P]/dt = k_1[AB] = k_2[A][B]$$

$k_2 = k_1 k_d / (k_1 + k_d')$ k_2 is the effective bimolecular rate constant

$k_d' \ll k_1$, $k_2 = k_1 k_d / k_1 = k_d$ diffusion controlled

$k_1 \ll k_d'$, $k_2 = k_1 k_d / k_d' = K k_1$ activation controlled

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.

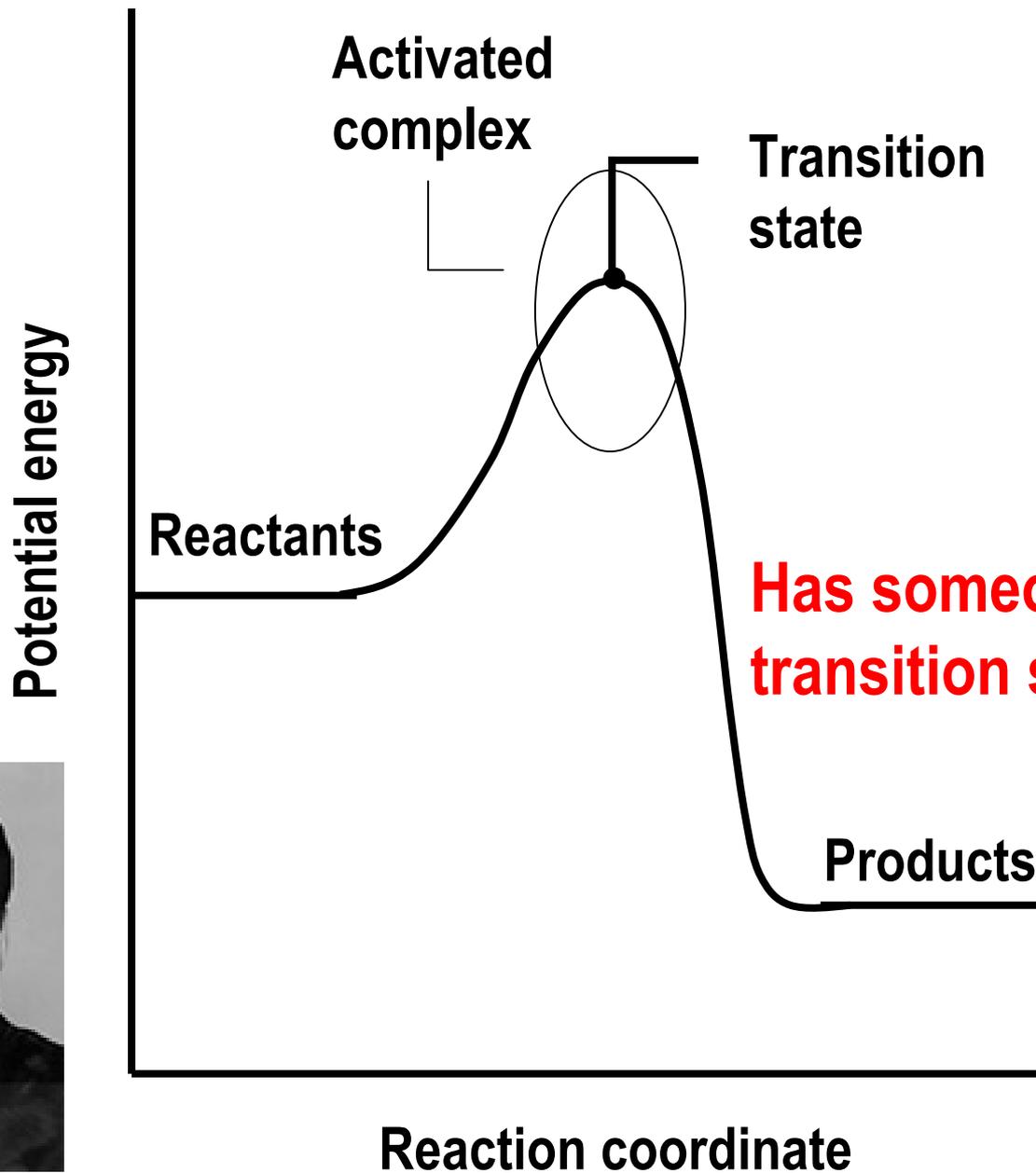
The theory is applicable essentially to gaseous reactions

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



A 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 $[AB^\ddagger]$

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

\therefore Rate of reaction = $[AB^\ddagger]$ x frequency of decomposition of AB^\ddagger

$$K_{eq}^\ddagger = [AB^\ddagger] / [A] [B]$$

$$[AB^\ddagger] = K_{eq}^\ddagger [A] [B]$$

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.

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

$$\begin{aligned} \text{Rate of reaction} &= [AB^\ddagger] \nu \\ &= K_{eq}^\ddagger \nu [A] [B] \end{aligned}$$

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

∴ The vibration of low frequency will decompose the activated complex.

∴ Energy of vibration $E = h\nu$

$$\nu = E/h = k_B T/h$$

In a classical sense, the average energy of such a vibrational degree of freedom, $k_B T$ (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.

Eyring equation

$$k = k_B T / h K_{eq}^\ddagger (C^\circ)^{1-m}$$

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.

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



Dimensionless

k is in s^{-1} for 1st order

for second order, $\text{L mol}^{-1} \text{s}^{-1} = \text{s}^{-1} (C^\circ)^{-1}$

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

K_{eq}^\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_{eq}^\ddagger can be interpreted in terms of ΔG^\ddagger , ΔS^\ddagger and ΔH^\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.

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

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

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

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

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 ΔH^\ddagger .

We need to find relation between ΔH^\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 .

ΔE^\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 $E_a = \Delta H^\ddagger + RT - P\Delta V^\ddagger$

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

$$\therefore P\Delta V^\ddagger = \Delta n^\ddagger RT$$

For ideal gases, it becomes

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

ΔV^\ddagger is volume change and Δn^\ddagger is the change in number of moles from initial state to the activated state.

For bimolecular reaction

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

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

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

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

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

Note this e^2

ΔS^\ddagger can be calculated from k_2 & E_a .

This term 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)

ΔS^\ddagger negative means activated complex is more ordered than the reactants and A will have smaller value

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

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

And reaction will be slower.

Positive ΔS^\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

$\text{CH}_3 + \text{D}_2 \rightarrow \text{CH}_3\text{D} + \text{D}$, the rate constant is given by

$k = 2 \times 10^9 \exp^{-6389/T} \text{ M}^{-1}\text{s}^{-1}$ over the temperature range 300 to 626 K
calculate enthalpy and entropy of activation for this reactions at 300K.

Since $n = -1$.

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

$$= 6389 \times 8.314 - 2 \times 8.314 \times 300$$

$$= 48.1 \text{ kJ/mol}$$

$$\exp \Delta S^\ddagger/R = AhC_0/k_B T e^2$$

$$= ((2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) (6.63 \times 10^{-34} \text{ Js}) (1\text{M})) / ((1.38 \times 10^{-23} \text{ JK}^{-1}) (300\text{K}) e^2)$$

$$= 4.35 \times 10^{-15}$$

$$\therefore \Delta S^\ddagger = - 83.50 \text{ JK}^{-1} \text{ mol}^{-1}$$

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 $\text{H}_\text{A}-\text{H}_\text{B}$ results in the formation of $\text{H}_\text{B}-\text{H}_\text{C}$ 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.

