Lecture notes on

Chemical Kinetics

for 2nd Semester students
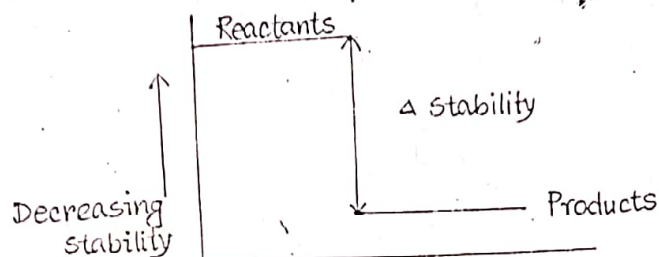
by

Dr Subhra Mishra

Reactants $\longrightarrow$ Products

A chemical reaction proceeds when the products are more stable than the reactants. i.e. the larger Δstability is in the diagram the greater the conversion of reactant to products.

The free energy change during a reaction at a particular temp. T is given by

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

$\Delta H \equiv$ Heat constant, which is the quantity of heat released or absorbed when a mole of reactant is converted to a mole of product. Enthalpy is associated with bonding. If stronger bonds are formed in a reaction ΔH is negative and the reaction is exothermic. A reaction with $\oplus$ve ΔH is endothermic.

$\Delta S \equiv$ Entropy factor, a measure of degree of disorder of a system.

It should be noted that a reaction proceeds in the forward direction only when ΔG is $\ominus$ve. A system is more stable if it has maximum entropy and minimum energy.

When all the substances are their standard states (at 25°c and 1 atmosphere pressure). The equation may be written as -

$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta G° = G° \text{ (Products)} - G° \text{ (Reactants)}$$

The relationship between the equation, equilibrium equlⁿ constant and $\Delta G°$ is given by

$$\Delta G° = - RT \ln k.$$

* Though negative value for ΔG is a necessary condition for occurance of a reaction under the given set of conditions, but this value tells us nothing about how fast the starting materials are go to products. Thus for oxidation of cellulose

$$(C_6H_{10}O_5)n + 6nO_2 \rightleftharpoons 6nCO_2 + 5n H_2O$$
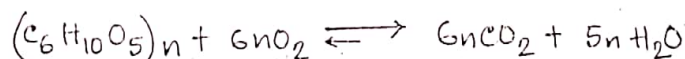
ΔG is negative in large magnitude so the equi^m lies over completely to the product. But a news paper can be read in the air for long periods of time without it noticially fading away to gaseous products. The rate of the conversion is extremely slow. The reaction is speeded up at higher temperature. The conversion of starting materials into products is rarely if a mere run down hill (fig·A), there is generally a barrier to be overcome on route (fig·B).
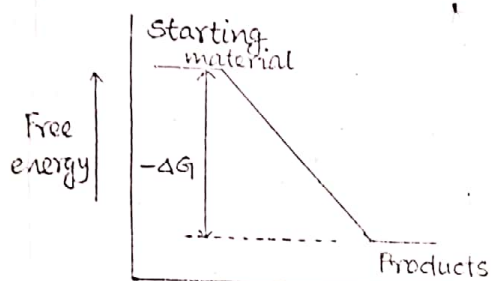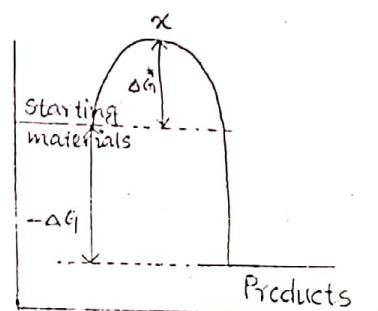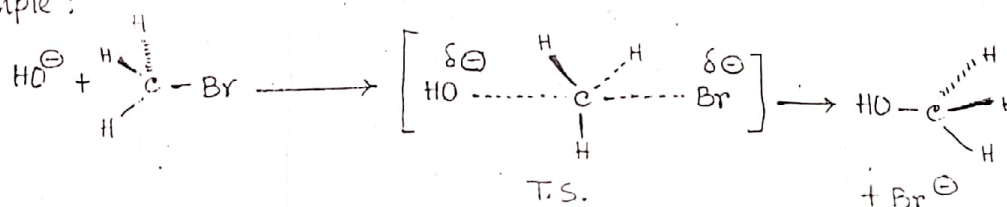

fig - A   fig - B

The position x in the energy profile above corresponds to the least stable configuration through which the starting materials pass during their conversion into the products and is generally referred to as an activated complex or transition state, that can not be detected or even isolated.

Example :

T.S.

The height of the barrier $\Delta G^{\ddagger}$ is called the free energy of activation for the reaction. (The higher it is the slower the reaction).

Thus the difference in energy of the isolated reactants and the maximum energy structure which the system ~~pares~~ passes through on the path of to products is the activation energy of the reaction. The maximum energy corresponds to a definite structure called the transition state. The measure of the progress of reaction from reactants to products is the reaction co-ordinate.

Energy profile diagram for a one step process :

Transition state

activation energy

ΔG

Reactants

Products

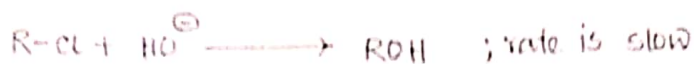$\longrightarrow$ R.C.
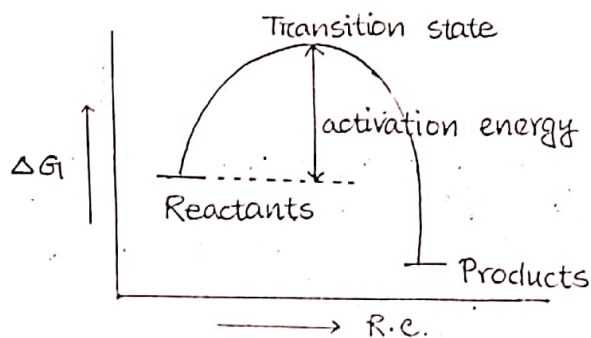
Energy diagram for a two step process :

Many organic reaction proceed through intermediates which may or may not posses enough stability to permit isolation. There are two transition states in a two steps reaction and it will have one intermediate between reactants and products represented by a minimum in the energy profile diagram.

First transition state

Second transition state

$\Delta G^{\ddagger}$

Reactants

ΔG^{0}

Energy

Products

$\longrightarrow$ R.C.
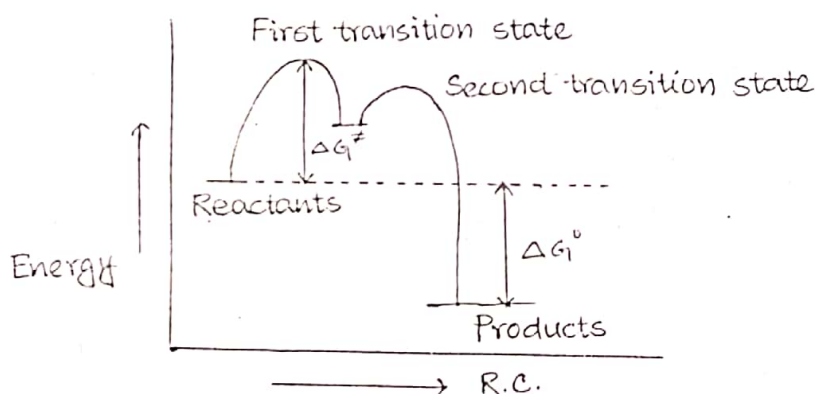
The deeper the depresion, the more stable will be the intermediate and conversely a shallow depression in the energy curve indicates a less stable intermediate. Although there are two transition states each with an energy higher than that of the intermediate, the over all rate of the reaction is reflected in the energy difference and the highest energy transition states. The step involving this transition state is often called the rate determining step (r.d.s.).

In the above cases the first step is r.d.s.

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Catalysis :

$$R\text{-}Cl + HO^{\ominus} \longrightarrow ROH \quad ; \text{ rate is slow}$$

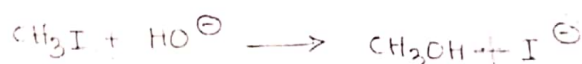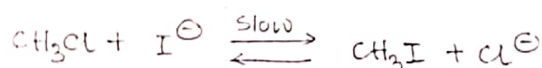$$R\text{-}Cl + HO^{\ominus} \xrightarrow{\text{KI}} ROH \quad ; \text{ rate is very fast}$$

A catalyst may be defined as a substance that increase the rate of the reaction without it self being consumed in the process. A catalyst increase the rate of the reaction by providing an alternative path from reactants to products with a lower energy transition state.

Methyl chloride reacts with the hydroxide ion in a one step process and as expected the rate depends on $\Delta G^{\neq}$.

$$CH_3Cl + HO^{\ominus} \longrightarrow CH_3OH + Cl^{\ominus}$$

Addition of iodine ion to the reaction mixture provides an alternative path consisting of a two step mechanism in which methyl iodide as an intermediate.

$$CH_3Cl + I^{\ominus} \underset{\longleftarrow}{\overset{\text{slow}}{\longrightarrow}} CH_3I + Cl^{\ominus}$$

$$CH_3I + HO^{\ominus} \longrightarrow CH_3OH + I^{\ominus}$$

Since iodide ion is both the excellent nucleophile and excellent leaving group, the transition states of each step $(\Delta G^{\neq}_{I}$ and $\Delta G^{\neq}_{II})$ have lower energy than that for the one step process.
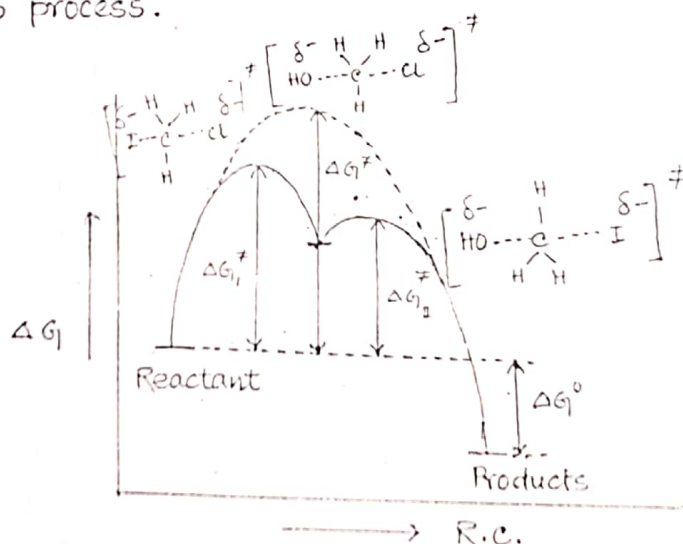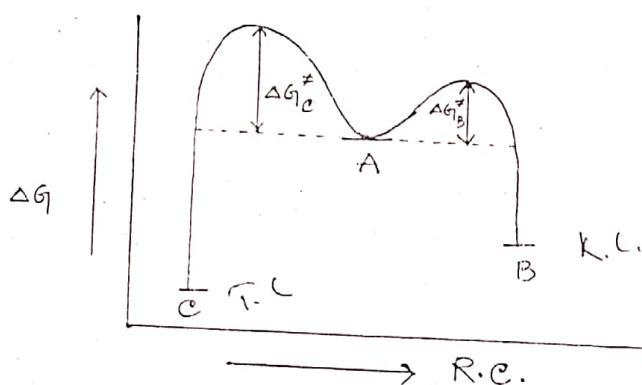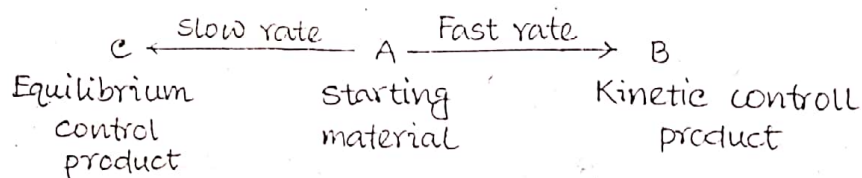
Kinetic vs. Thermodynamically controlled Reaction :

When a starting material may be converted into two or more alternative products, the proportions in which the alternative products are formed are often determined by their relative rate of formation. The faster a product is formed the more of it there will be in the final product mixture, this is known as kinetic controll.
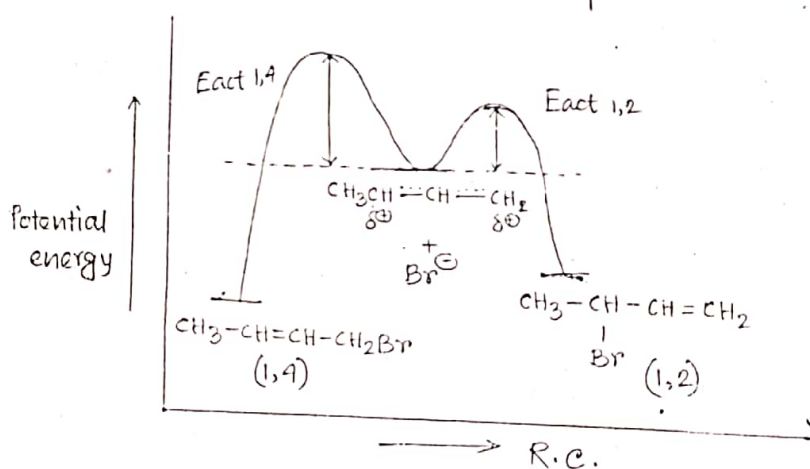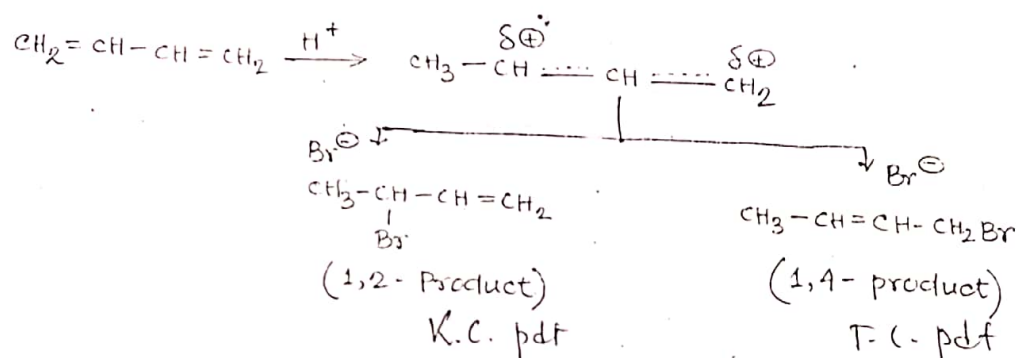
If one or more of the alternative reactions is reversible, or if the products are readily inter convertible directly under the conditions of the reaction, the composition of the final product mixture may be dictated not by the relative rates of formation of the different products, but by their relative, thermodynamic stabilities in the reaction system. We are then seeing thermodynamic or equ^m control.

Thus :

$$C \xleftarrow{\text{Slow rate}} A \xrightarrow{\text{Fast rate}} B$$

Equilibrium Control product	Starting material	Kinetic controll product

ΔG vs R.C. diagram showing $\Delta G_C^{\ddagger}$, $\Delta G_B^{\ddagger}$, A, B (K.C.), C (T.C.)

* **Examples :**

① The reactions of hydrogen bromide with 1,3-butadiene serve as a striking illustration of the way that the out come of a chemical reaction can be determined, in one instance, by relative rates and in another, by the relative stabilities of the final products. At the lower temperature, the relative amounts of the products of the addition are determined by the relative rates at which the two addition are determined by the relative rates at which the two additions occur. 1,2 addition occurs faster so the major product is 1,2 addition product. At the higher temperature, the relative amounts of the products are determined by the position of an equilibrium. The 1,4-addition product is the more stable, so it is the major product.

$$CH_2 = CH - CH = CH_2 \xrightarrow{H^+} CH_3 - CH \cdots CH \cdots \overset{\delta\oplus}{CH_2}$$

$$CH_3 - CH - CH = CH_2$$
$$\qquad\quad |$$
$$\qquad\quad Br$$

(1,2- Product)
K.C. pdt

$$CH_3 - CH = CH - CH_2 Br$$

(1,4- product)
T. C. pdf

② Rate Thus the nitration of methyl benzene is found to be Kinetically controlled, where as Friedel crafts alkylation of the same species is often thermodynamically controlled.

③ Sulphonation of napthalene with concentrated H_2SO_4 at 80°C is Kinetically controlled where as at 160°C it is thermodynamically controlled.
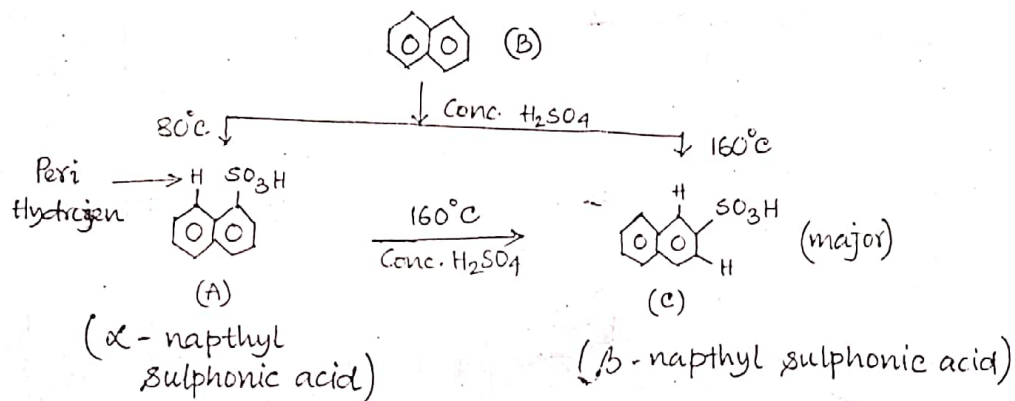
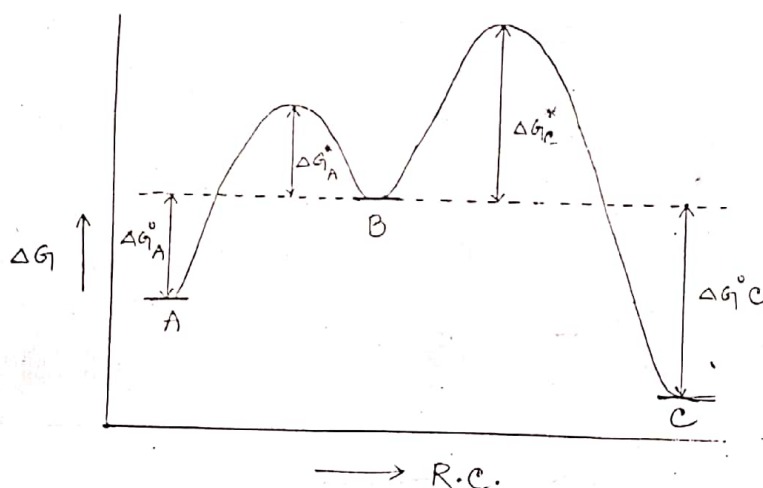*** Draw the energy profile diagram for the reactions

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} C$$
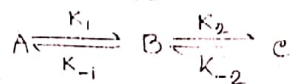
i) Which is the kinetically controlled product?
ii) Which one is the major product after equilibrium of the reaction?
iii) Give a concrete illustration of the above reaction.

Sol^n:

i) A is the kinetically controlled product.
ii) C is the major product after equilibrium of the reaction.
iii)

(B)

↓ Conc. H_2SO_4

80°C ⌐————————————————————————┐ 160°C

Peri ——→ H SO$_3$H
Hydrogen

(A)
(α-napthyl sulphonic acid)

$\xrightarrow[\text{Conc. } H_2SO_4]{160°C}$

SO$_3$H (major)

(c)
(β-napthyl sulphonic acid)

Energy profile diagram :

ΔG ↑

ΔG_A^0

ΔG_A^*

ΔG_C^*

B

ΔG_C^0

A

C

——→ R.C.