

## B.Sc. (Hons) Part II

### CHEMICAL KINETICS

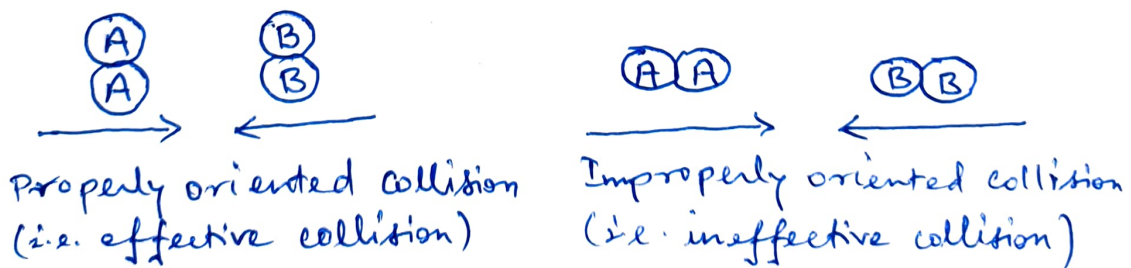
Paper : III A Physical Chemistry

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(Continued from page 08)

The molecules must collide with correct Orientation : Only energy factor can not explain the relation between rate of reaction and collision because in many cases it was found that the rate is not too high even if a large number of active molecules collide in the reacting mixture.

This fact was explained on the basis of orientation factor, because only those collisions among active molecules are effective which are properly oriented. i.e. the reactant molecules must collide with favourable orientation. The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming bonds. This can be shown in below figure.



From the above discussions one can say that "only the molecules colliding with kinetic energy greater than the activation energy ( $E_a$ ) and with correct orientation can cause reaction.

Hence, the rate of a reaction is given by the number of molecules colliding per second per unit volume and the fraction of molecules

that possess sufficient activation energy. Thus, according to collision theory, the rate of reaction is given by as

$$k = Z \cdot q \quad \text{--- (1)}$$

where  $Z$  is collision frequency (i.e. number of collisions per second between molecules) and  $q$  is the fraction of molecules which are activated.

On the basis of kinetic theory of gases, the value of  $q$  can be related to Boltzmann factor ( $e^{-E_a/RT}$ ) as follows:

$$q = e^{-E_a/RT} \quad \text{--- (2)}$$

Therefore, the rate constant becomes

$$k = Z \cdot e^{-E_a/RT} \quad \text{--- (3)}$$

This theoretical equation can be tested by comparing the calculated value of  $k$  with the experimental value for a number of reactions. For the simple gaseous reactions, the agreement between the two values is fairly good. But for reactions between complicated molecules, the observed rate is found to be much smaller than the theoretical rate, sometimes by a factor of  $10^5$ .

This discrepancy is explained by the fact that the colliding molecules are treated as hard spheres having no internal energies. Again, the spherical model ignores the dependence of the effectiveness of a collision on the relative orientation of the colliding molecules. Also, the activation energy has been treated as though it were related entirely to translational motion, ignoring the effect of rotational and vibrational motion. For these reasons the collision theory is applicable only to reactions between very simple gaseous molecules.

Thus, the above theoretical equation (3) is modified as



$$k = p \cdot Z \cdot e^{-E_a/RT}$$

(10)

(4)

where  $p$  is called the probability factor, or steric factor or orientation factor and decides the number of effective collisions.  $p$  is a measure of discrepancy between simple collision theory and the experimental results.

### Demerits of Collision Theory :-

- (i) This theory is applicable to simple gaseous reactions only, also for solutions of simple molecules.
- (ii) It is valid for simple bimolecular reactions. For reactions involving complex molecules, the experimental rate constants are quite different than calculated values.
- (iii) It does not consider the energy changes taking place during breaking and formation of bonds.
- (iv) It neglects the vibrational and rotational energies of molecules.
- (v) Abnormally high values of rate constants that are sometimes observed can not be properly explained on the basis of the arguments of collision theory.

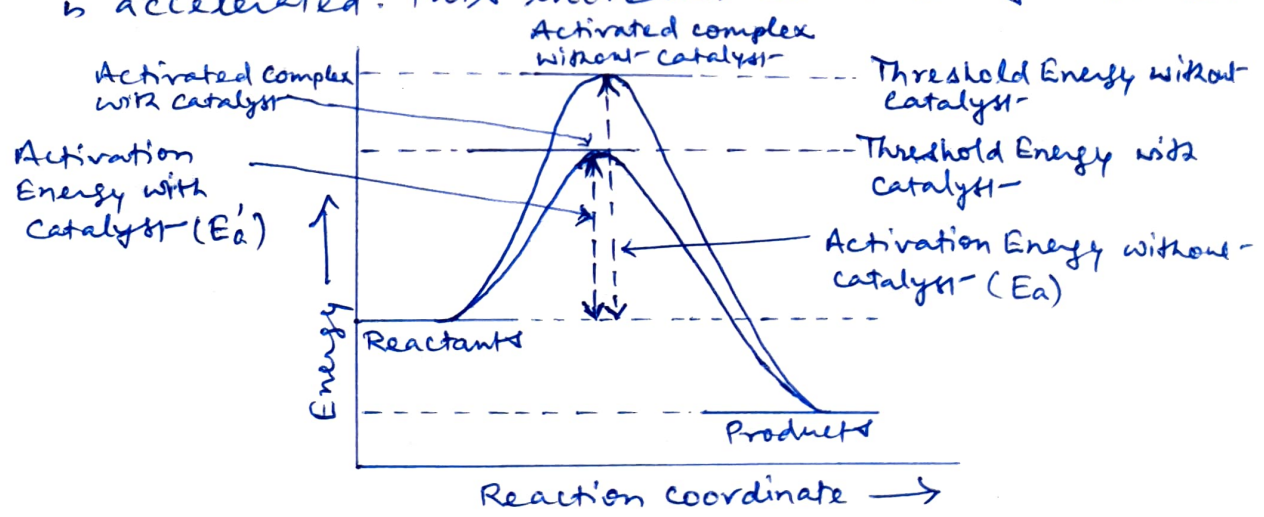
### Effect of Catalyst on Reaction Rates :-

A catalyst is a substance which alters (may increase or decrease) the rate of a chemical reaction but itself remains chemically or quantitatively unchanged at the end of the reaction. The process is called catalysis.

According to the collision theory of reaction rates, the colliding molecules (or inactive molecules) do not react unless they attain a <sup>certain</sup> minimum amount of energy, i.e. activation energy,  $E_a$  and become active molecules.

Only active molecules may collide effectively to yield products. For this active molecules must cross the energy barrier which is equal to threshold energy. In other words we can say that the total energy of reactant molecules showing active and effective collisions is known as threshold energy. Thus as the number of active molecules increases, the rate of reaction increases due to increased number of effective collisions. The active molecule on effective collision first forms an activated complex. As a result of breaking and forming of new bonds, the activated complex dissociates to give product molecules.

When a catalyst is added in a chemical reaction, it lowers the activation energy and gives a new reaction pathway with a lower energy barrier. Since the energy barrier is reduced in magnitude, number of active molecules increases and reaction is accelerated. This increases the rate of the reaction.



Thus large number of effective collisions occur in the presence of the catalyst than would occur at the same temperature without the presence of the catalyst. In this way the presence of a catalyst makes the reaction go faster, other conditions remaining the same.

To be continued - - - -