

# Unit - Chemical Dynamics

## Theories of reaction rates

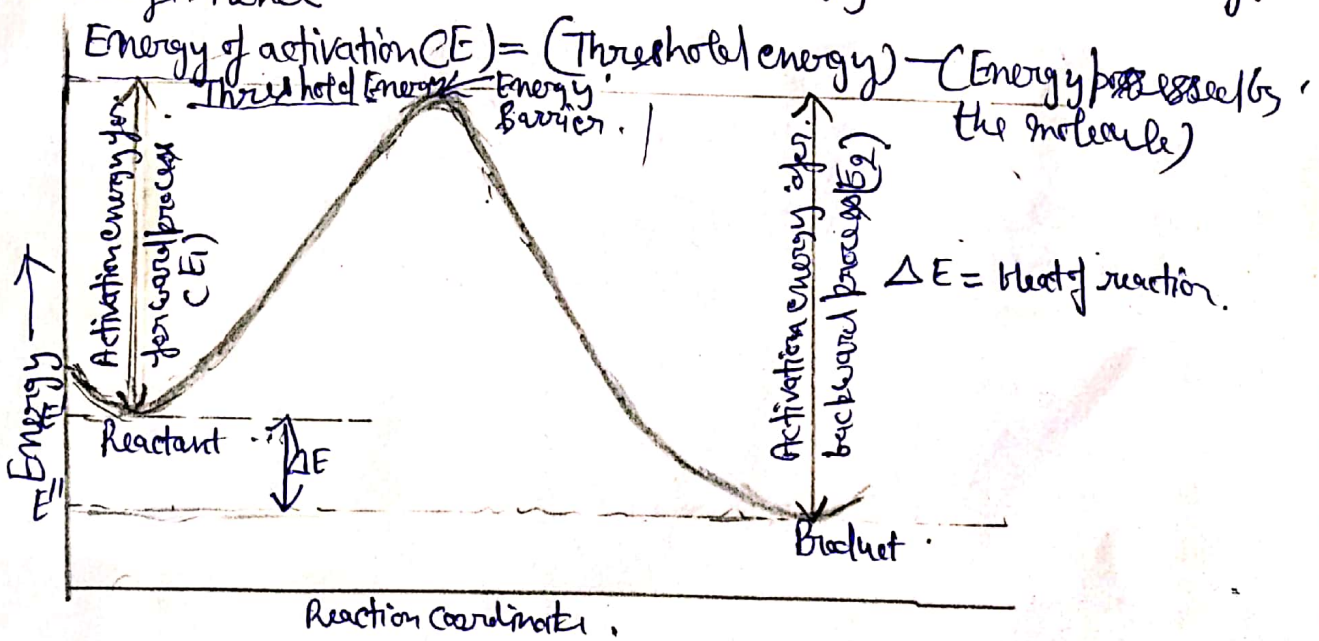
There are two important theories of reaction rates are.

- (1) Collision Theory.
- (2) Activated complex theory.

### Collision Theory of reaction rates

#### Postulates of collision Theory

- (1) For a reaction to take place, the collisions between reacting molecules must occur.
- (2) All the collisions do not lead to product formation.
- (3) Only those collisions result in chemical reaction (i.e. product formation) in which the colliding molecules possess a certain minimum amount of energy, called 'threshold energy'. Hence 'threshold energy' is defined as the minimum amount of energy which must be associated with the molecules, so that their mutual collisions result in product formation. The collisions which yield product formation are called effective collisions. The activation of molecules can also be expressed in terms of energy activation, so that the 'energy of activation' is defined as the excess energy that the reacting molecules acquire to attain the threshold energy, in order to undergo chemical change. Hence



Concept of energy barrier and energy of activation.

- ① The colliding molecules must be properly oriented, if the reaction is to take place. If these molecules are not in proper orientation, product formation is not possible. The energy required for effective collisions between poorly oriented molecules is much more than the energy required for properly oriented collisions.

### Mathematical Treatment of Collision Theory for a Bimolecular Reaction

Let

$Z$  = Number of binary collisions per second between two identical molecules in 1 ml of gas.

$E$  = Energy of Activation of the process.

Then! Rate of reaction is given by

$$\frac{dx}{dt} = Z e^{-E/RT} \quad \text{--- (1)}$$

$$\text{But } \frac{dx}{dt} = k a^2 \quad \text{--- (2)}$$

where  $k$  = specific reaction rate.

$a$  = Concentration of the reactant.

From eqn (1) & (2) we get

$$k = \frac{Z}{a^2} e^{-E/RT} \quad \text{--- (3)}$$

$$k = Z \cdot e^{-E/RT} \quad \text{--- (4)}$$

In above eqn  $Z$  is called collision number or collision frequency. It is defined as the number of collisions per unit time suffered by any one particle in one ml of gas.

Equation (4) is called as the mathematical statement of Collision Theory.

Comparison of eqn (4) with Arrhenius eqn.

$$\text{Arrhenius eqn. is: } k = A e^{-E/RT}$$

where  $A$  = Frequency factor.

Eqn (4) is identical with Arrhenius eqn. if  $A = Z$ .

### Test of Collision Theory

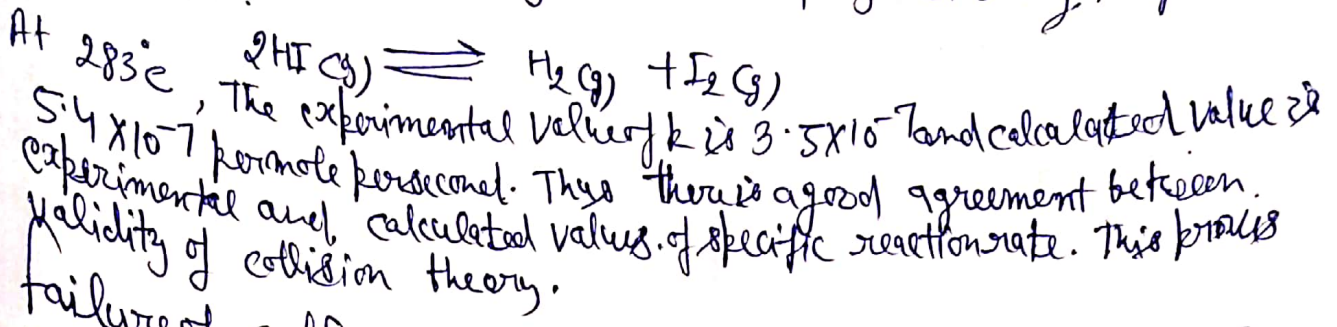
The eqn (4) of collision frequency can be tested, in two ways:

① The values of  $Z$  calculated from eqn (4) are compared with the experimental values - for a number of gas reactions.

② By comparing the specific reaction rate calculated from eqn (4) with the observed value

Contd.

~~At 283°C~~ The method may be illustrated by considering the following reaction:



Failure of Collision Theory: The Theory fails in many cases. For example,

- (1) The chain reactions proceed at a very fast rate which is much higher than the theoretical value calculated from collision theory.
- (2) The bimolecular polymerization of ethylene takes place at a rate which is slower than the theoretical value calculated from collision theory.

Modification of collision Theory:

There are several reactions where calculated and experimental values of  $k$  differ widely. In some cases the rate const. were found to be much smaller than the predicted ones, the discrepancy being much larger for complex molecules. Thus in order to account for the deviations, a factor  $P$  was introduced into eqn (4) as follows:

$$k = P Z C^{-E/RT} \quad \text{--- (5)}$$

where  $P$  is called steric factor, or probability factor.

The value of  $P$  varies from 1 to  $10^{-9}$ . In some cases  $P$  is as large as  $10^6$ .

Weakness of Collision Theory: The following are the weaknesses

- (1) The collision theory does not give any explanation for abnormally high rates of reactant molecules.
- (2) Collision theory fails to correlate steric factor  $P$  with the characteristics of reactant molecules.
- (3) Collision theory is unable to explain reversible and complicated reactions.

Causes of the Weaknesses of the Collision Theory.

The following are the reasons for the weakness of collision theory.

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- ① In collision theory, the mathematical calculations are based on the assumptions that molecules are elastic hard spheres. Such assumptions are true only in ideal gases.
- ② With larger molecules, many collisions would take place where vulnerable reactive parts would not be brought together, although molecules have high energy. In consequence many such collisions of activated molecules become infructuous, the steric factor  $P$  becomes much less than unity.
- ③ In the calculation for energy of activation, only translational energy has been considered. No account is taken of the internal motions of the reacting molecules. There may be contribution from rotational and vibrational motions towards energy of activation. If such contributions are appreciable, the observed rate of reaction would be greater than the calculated rate.
- ④ Collision theory is totally based on classical mechanism, which is very crude, and requires modifications. For the above reasons correct theoretical prediction for reaction rates is difficult in case of reactions with large molecules.