

Concept of Activation Energy

The minimum amount of energy required for reacting molecules to convert into product is called threshold energy. Energy associated with molecules before reaction under ordinary condition (room temperature) is called average kinetic energy which is less than threshold energy. So, extra energy must be supplied to activate molecules for the reaction.

The additional amount of energy which is supplied over average energy of reacting molecules to convert into product is called activation energy.

Then,

Threshold Energy = Activation energy + Average energy

$$E_T = E_a + E_{av}$$

$$\therefore E_a = E_T - E_{av}$$

A reaction having lower activation energy occurs fast because large number of molecules will soon cross energy barrier. Similarly, reaction with higher activation energy occurs slowly. The reaction having activation energy zero is nearly explosive.

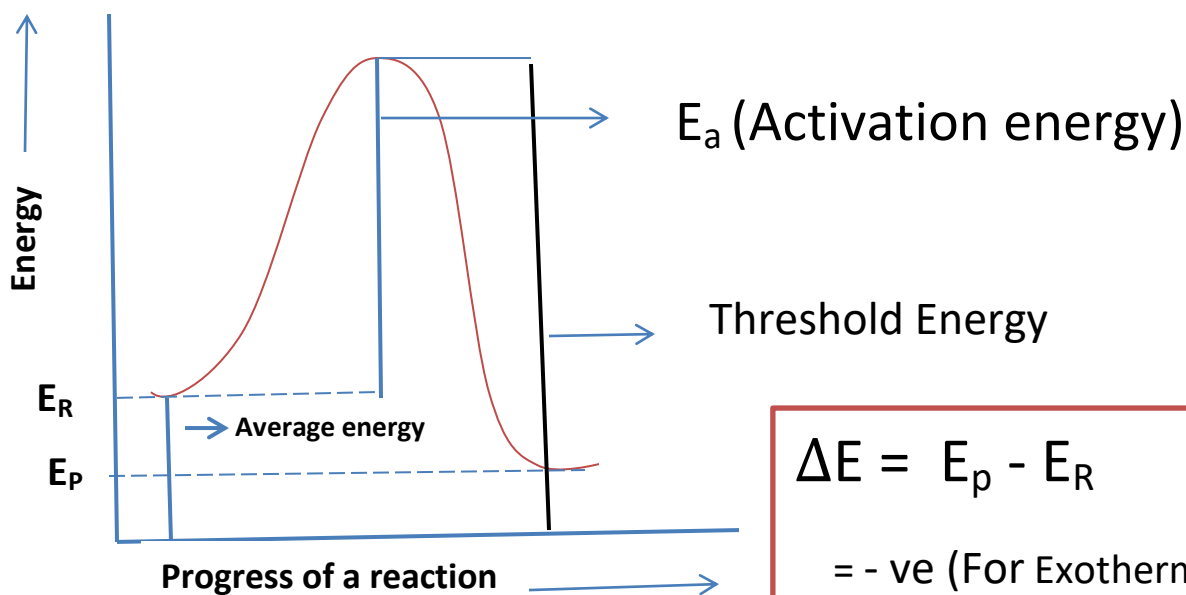


Fig: Energy profile diagram

$$\Delta E = E_p - E_R$$

= - ve (For Exothermic Reaction)

Arrhenius Equation:

The relationship between rate constant (K) and temperature of a system is given by the Arrhenius equation.

$$K = Ae^{-E_a/RT}$$

Where, E_a = Activation energy

K = rate constant

R = universal gas constant

A = Arrhenius factor and it is constant for a particular reaction

e = natural base

The Arrhenius equation can also be expressed in logarithmic form as,

$$\ln K = \ln A - \frac{E_a}{RT} \quad \text{-----} \quad 1$$

If K_1 and K_2 be the rate constants at temperature T_1 and T_2 respectively, the Arrhenius equation can be written in another form as:

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Q. For a first order reaction, the half-life at 328 K is 330 sec and that at 298 K is 1.69×10^4 sec. Calculate activation energy.

Q. The rate of most reactions doubles when the temperature is raised from 25°C to 35°C . Calculate the activation energy.

Calculation of activation energy (E_a) using Arrhenius Equation

In a slightly rearranged form equation 1 can be written as,

$$\log K = \log A - \frac{E_a}{2.303RT} \quad (\text{Dividing by } 2.303 \text{ on both sides})$$

$$\text{Or, } \log K = - \frac{E_a}{2.303RT} + \log A$$

This equation is in the form of $y = mx + c$. So, when $\log K$ is plotted against $\frac{1}{T}$, a straight line with y intercept $\log A$ and slope $= - \frac{E_a}{2.303R}$ is obtained and by knowing the value of slope and Universal gas constant (R), activation energy can be calculated.

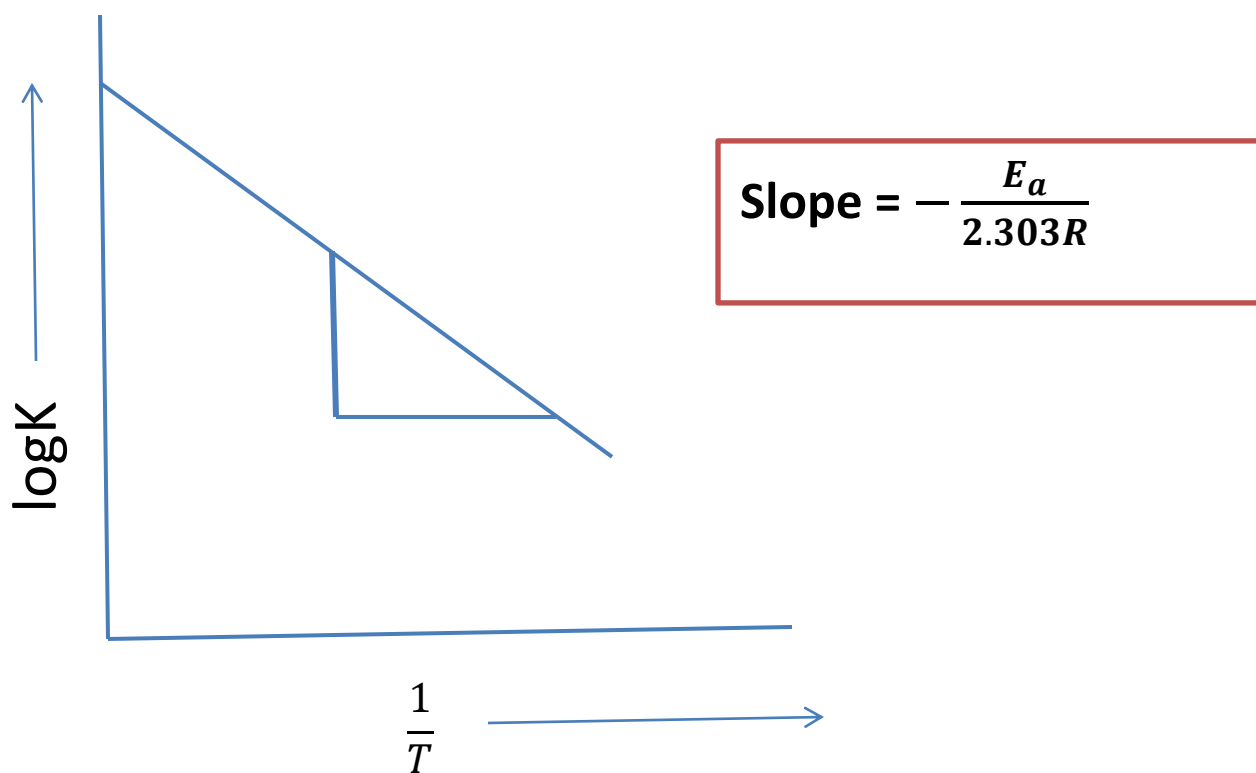


Fig: Plot of $\log K$ vs. $\frac{1}{T}$

Theories of reaction rate:

A) Collision theory

b) Activated complex theory

A) Collision theory

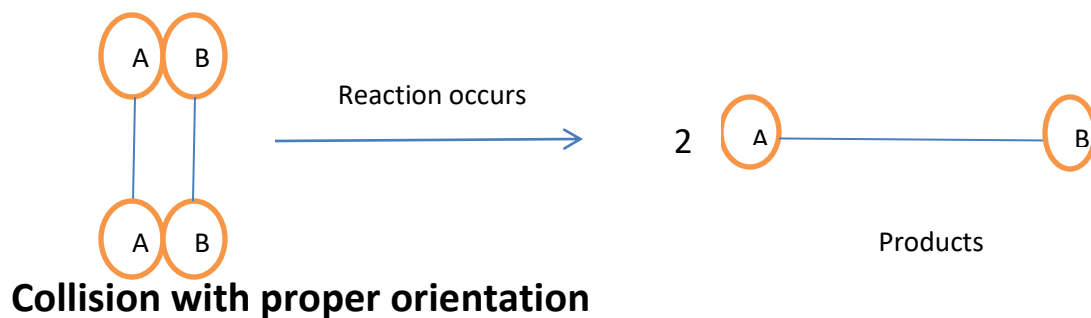
According to this theory, a chemical reaction takes place only by collision between the reacting molecules. Not all molecular collision can bring the chemical reaction, only the effective collision can bring about the chemical change. The effective collision is that molecular collisions which are capable to overcome threshold energy barrier. Two main criteria for reactions are:

- a) The colliding molecules must possess sufficient kinetic energy to cause a reaction.
- b) The reacting molecules must collide with proper orientation

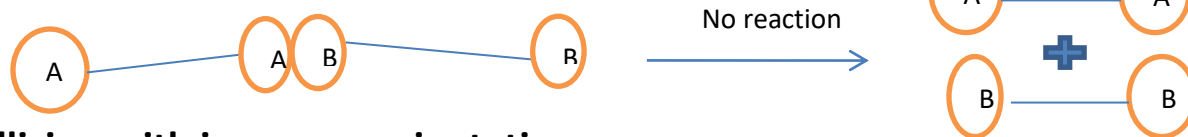
The concept of proper orientation can be illustrated by considering the following reaction



i) Collision with proper orientation



ii) Collisions with improper orientation



Collision with improper orientation

According to collision theory, the rate of a reaction can be written as.

$$\text{Rate} = f \times p \times z$$

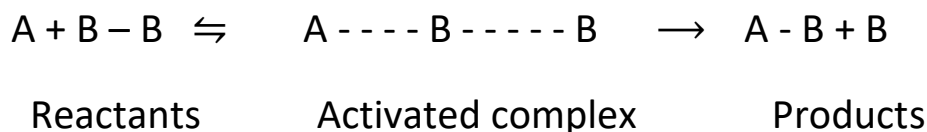
Where, f = fraction of molecules which possess sufficient energy to react

p = probable fraction of collision with effective orientation

z = collision frequency

B) Activated Complex Theory

Activated complex theory posits that, the reactants molecules are transformed into high energy containing intermediate complex before changing into product and such intermediate complex associated with high energy is called activated complex or transition state. The rate of a reaction is given by rate of decomposition of activated complex to products.



The activated complex state has very short life span and breaks immediately into reactants or products to acquire stable state of lower energy. The concept of activated complex theory can be illustrated by the following energy profile diagram.

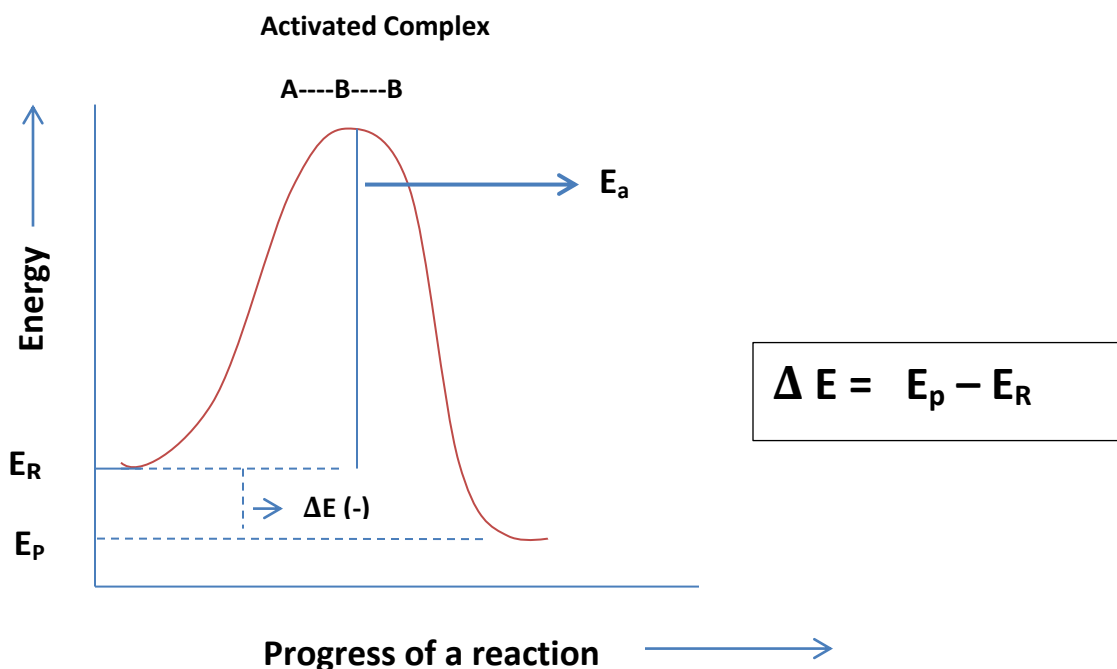


Fig: Energy profile diagram showing activated complex for the reaction ($A + B_2 \rightarrow AB + B$)

(Important for examination)

Factors affecting rate of a reaction

The rate of a reaction depends upon the following factors:

a) Particles size of reactants

The rate of a reaction depends on particle size or surface area of reactants. This is because as particle size decreases, surface area increases and more area is exposed to react. Thus, rate of a reaction increases. For example: Dilute HCl reacts faster with powdered calcium carbonate than marble chips.

Q. Why powdered coals burns faster than lump of a coal?

It is because as particle size of coal decreases, surface area increases and more area of coal is exposed to burn. Thus, powdered coals burn faster than lump of coal.

Q. why powdered sugar dissolves faster than sugar cube?

It is because as size of sugar particles decreases, surface area increases and more area of sugar is exposed to solvent and dissolves more quickly than sugar cube.

b) Nature of reactants

The reaction of ionic compound in solution state proceeds with higher rate than the reaction of covalent compounds. It is because, in solution state, ionic compounds are completely ionized before the reaction and hence their reactions are fast whereas reactions of covalent compounds are molecular in nature and slow.

c) Effect of concentration

In general, the rate of reaction increases with increase in concentration of reactants. It is because with increase in concentration, more number of molecules comes into contact and number of effective collision also increases. Thus, with increase in concentration of reactants the rate of reaction also increases. For example, the reaction of marble chips is faster with Conc. HCl than dilute HCl and evolution of CO_2 is faster and high in Conc. HCl.

d) Effect of catalyst

The rate of chemical reaction depends on nature of catalyst. The positive catalyst accelerates the rate of a reaction while negative catalyst retards the rate of a reaction. A catalyst is chemical substance that increases or decreases reaction rate without itself undergoing any chemical change at the end of reaction. In general, catalyst is used

to increase rate of a reaction. This is because the reaction follows the alternative pathway having lower activation energy. This can be shown by following energy profile diagram.

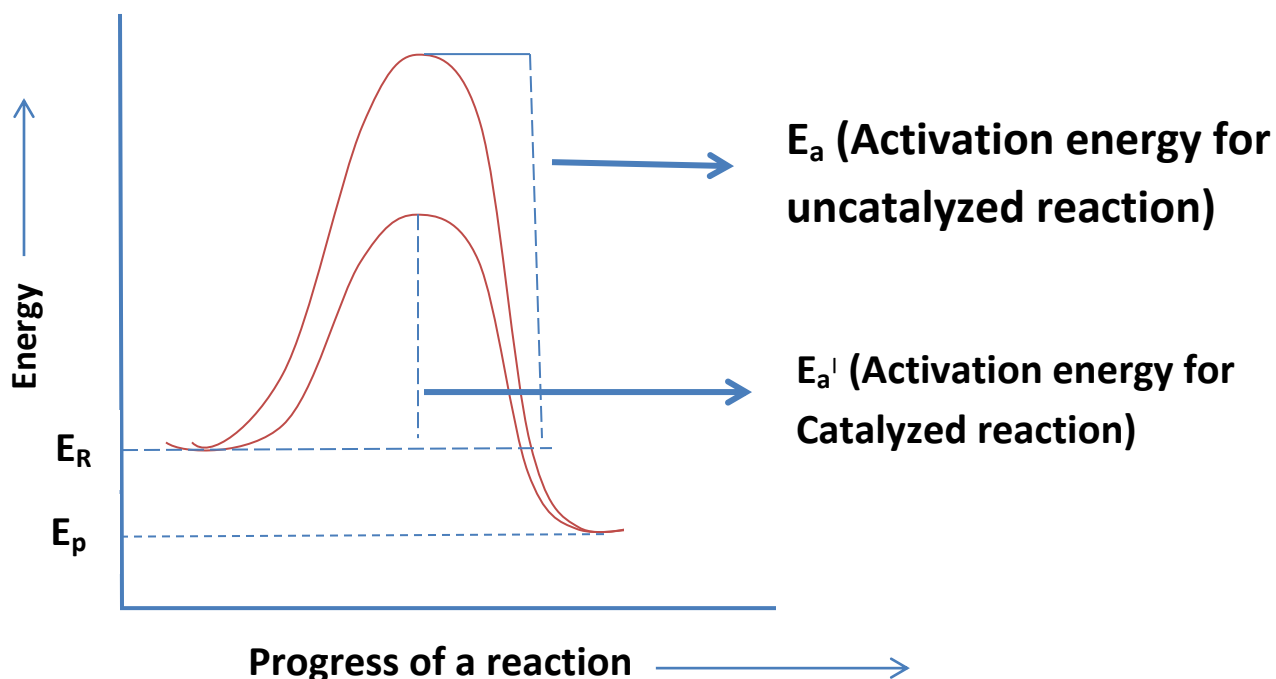


Fig: Energy profile diagram for uncatalyzed and catalyzed reactions

e) Effect of temperature

The rate of a reaction increases with increase in temperature. This is because as temperature increases, the kinetic energy of molecules increases which in turn increases no. of effective collisions. Hence, rate of reaction also increases. It is found that ,in most of the cases, for each 10°C rise in temperature rate of reaction increase by 2 to 3 times .

Q.1 A first order reaction undergoes 40 % completion in 8 minutes. Calculate the time required for 90% completion of the reaction.

Q.2 What is the half-life of a radioactive element if 75 % of a given sample of the substance disintegrates in 60 min?

Q.3 Find the two third life ($t_{2/3}$) of first order reaction in which $K = 5.48 \times 10^{-14} \text{ S}^{-1}$.