

CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED NOTES OF CHAPTER -04)

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4. CHEMICAL KINETICS

Half life of a first order reaction

For a first order reaction, $k = \frac{2.303 \log[R]_0}{t [R]}$

When $t = t_{1/2}$, $[R] = [R]_0/2$

Substitute these values in the above equation

$$k = \frac{2.303 \log[R]_0}{t_{1/2} [R]_0/2}$$

$$\text{Or, } t_{1/2} = \frac{2.303 \log 2}{K} = \frac{2.303 \times 0.3010}{K}$$

$$\text{Or, } \boxed{t_{1/2} = \frac{0.693}{k}}$$

Thus for a first order reaction, half-life period is constant. i.e., it is independent of initial concentration of the reacting species.

Pseudo first order reaction

These are reactions which appear to follow higher order but actually follow first order kinetics.

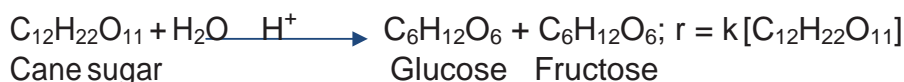
In these reactions the concentration of one of the reactants is large excess and so its change in concentration does not affect the rate of the reaction.

e.g. 1. Hydrolysis of ester (ethyl acetate)



Here the concentration of water does not change during the reaction.

2. Inversion of cane sugar



Rate of reaction and Temperature

Most of the chemical reactions are accelerated by increase in temperature. It has been found that for a chemical reaction, when the temperature is increased by 10° , the rate of the reaction and the rate constant is nearly doubled. The ratio of the rate constants of a reaction at two temperatures differing by 10° is called temperature coefficient.

i.e., Temperature coefficient = $\frac{\text{Rate constant of the reaction at } (T + 10)\text{K}}{\text{Rate constant of the reaction at } T \text{ K}}$

Rate constant of the reaction at T K

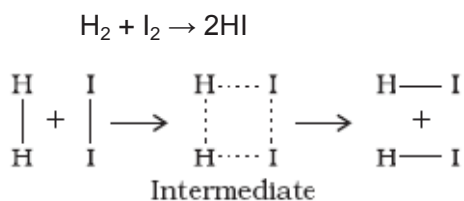
The temperature dependence of the rate of a chemical reaction can be accurately explained by **Arrhenius equation**. The equation is:

$$k = A e^{-E_a/RT} \dots \dots \dots (1)$$

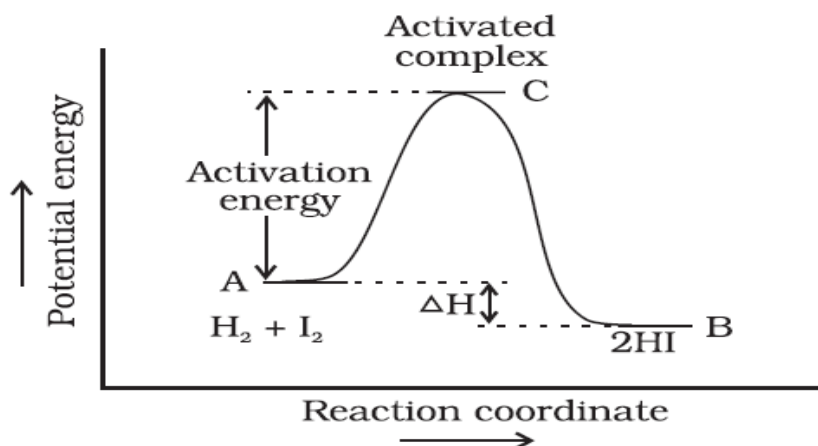
Where *A* is a constant called the Arrhenius parameter or the frequency factor or the pre-exponential factor. It is constant for a particular reaction. *R* is the universal gas constant and *E_a* is activation energy measured in joules/mole (J mol⁻¹).

According to Arrhenius, a chemical reaction occurs by the collision of reactant molecules. All the molecular collisions are not effective. For effective collision, the colliding molecules should have a minimum kinetic energy called **activation energy**. When such molecules collide, an unstable intermediate called **activated complex** is formed, which decomposes to form products.

For e.g. the reaction between H₂ and I₂ to form HI takes place in the following steps.

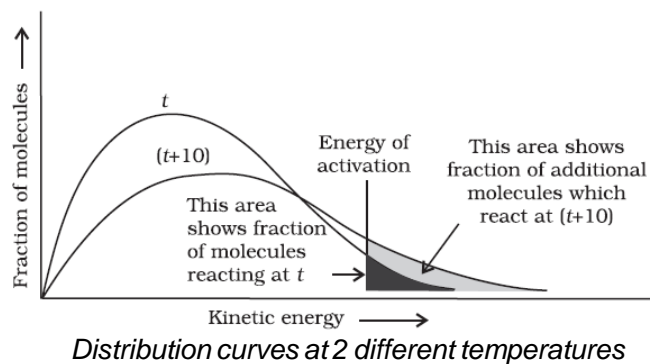
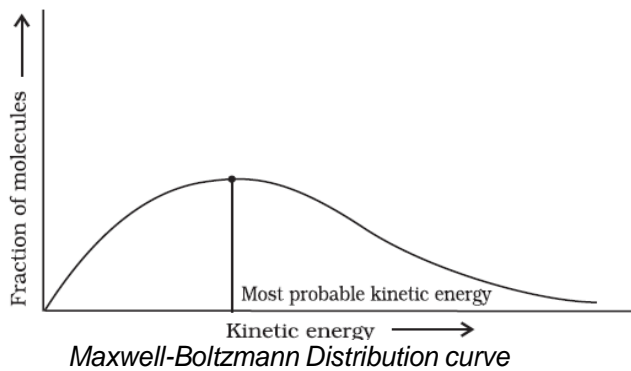


If we plot a graph between potential energy and the progress of reaction, we get the following graph.



Reaction coordinate represents the profile of energy change when reactants change into products.

In a chemical reaction, all the molecules in the reacting species do not have the same kinetic energy. Ludwig Boltzmann and James Clark Maxwell calculated the distribution of kinetic energy among molecules. They plotted a graph between the fractions of molecules with a given kinetic energy against kinetic energy. This plot is known as Maxwell- Boltzmann distribution curve of molecular energies.



The peak of the curve corresponds to the **most probable kinetic energy**. It is the kinetic energy possessed by maximum fraction of molecules.

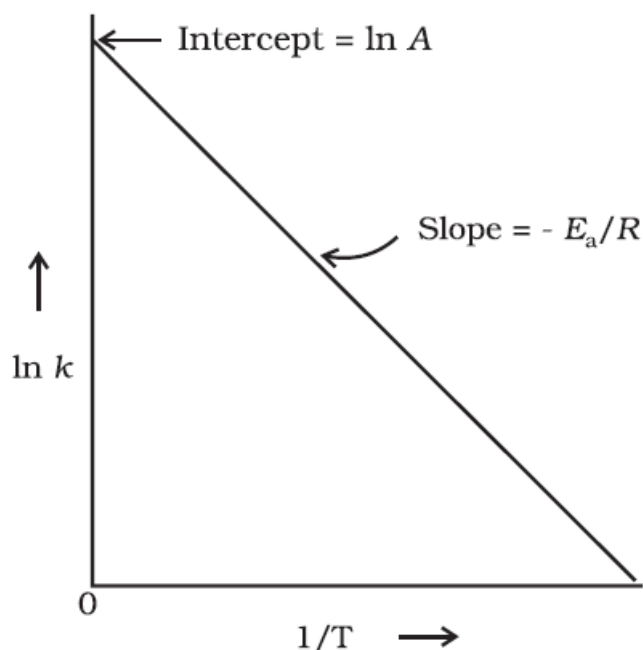
When the temperature is raised, the maximum of the curve moves to the higher energy value and the curve spreads to the right. That is the fraction of molecules with activation energy increases (almost doubled).

At normal temperature the fraction of molecules having energy equal to or greater than activation energy is very low. As the temperature increases, the fraction of molecules having energy equal to or greater than activation energy increases and hence the rate of reaction also increases.

In the Arrhenius equation the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a .

Taking logarithm on both sides of equation (1), we get $\ln k = -\frac{E_a}{RT} + \ln A$

This equation is of the form $y = mx + c$, equation for a straight line. So if we plot a graph between $\ln k$ against $1/T$, we get a straight line with slope $= -E_a/R$ and the y-intercept $\ln A$



If k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 , then

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \dots\dots\dots(2) \quad \text{and}$$

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \dots\dots\dots(3)$$

Equation (2) – (3) gives,

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$
$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

From this equation we can calculate the value of activation energy (E_a), by knowing all other values.

Effect of Catalyst

A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change. The action of the catalyst can be explained by **intermediate complex theory**. According to this theory, a catalyst participates in a chemical reaction by forming an intermediate complex. This is unstable and decomposes to yield products and the catalyst.
