

$$\log \frac{10}{a-x} = \frac{8.02 \times 10^{-5} \times 9.6 \times 60 \times 60}{2.303}$$

$$\log \frac{10}{a-x} = \frac{2.77171}{2.303}, \quad \frac{10}{a-x} = 15.9$$

$$\frac{a-x}{\text{(amount left)}} = \frac{10}{15.9} = 0.625 \text{ g}$$

$$(b) \quad t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$t = \frac{2.303}{8.02 \times 10^{-5}} \log \left(\frac{5.0 \times 10^{10}}{1.0 \times 10^8} \right) = \frac{2.303 \times 2.698}{8.02 \times 10^{-5}}$$

$$= 77503 \text{ s} = 21.52 \text{ hr}$$

COLLISION THEORY

- According to this theory a chemical reaction takes place due to collision between the reacting molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).

All collisions are not effective, only a small fraction of the collisions produces a reaction. The collisions that actually produce the products are effective collisions.

In order to form product, the colliding molecules must have sufficient kinetic energy to undergo a chemical reaction, which is known as threshold energy and the minimum amount of energy which a reactant molecule requires to participate in a chemical reaction is called activation energy *i.e.*,

Threshold energy = Initial potential energy of reactant molecule + Activation energy

- Another factor which enhances the effectiveness of the collision is correct orientation *i.e.*, the reacting molecules must collide in a proper way.
- Rate constant of reaction = $Z \times f \times P$

$$\therefore k = Z \times f \times P \quad \dots(i)$$

where Z = collision frequency, f = fraction of effective collision and P = orientation factor.

where f is given by : $f = e^{-E_a/RT}$

Substituting the value of f in equation (i) we get

$$k = PZe^{-E_a/RT}$$

ARRHENIUS EQUATION

- Arrhenius proposed a quantitative relationship between rate constant and temperature as $k = Ae^{-E_a/RT}$

k = rate constant, A = pre-exponential factor (called frequency factor),

E_a = activation energy, T = temperature

- Pre-exponential factor (A) is a constant specific to a particular reaction. This factor is related to number of binary molecular collision per second per litre.

Calculation of Activation Energy

- The minimum energy that the reacting molecule must possess before undergoing a reaction is called activation energy.

$$k = Ae^{-E_a/RT} \text{ (Arrhenius equation)}$$

$$2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

$$\log k = \log A - \frac{E_a}{2.303R}$$

When $\log k$ is plotted against

$$1/T, \text{ slope} = -\frac{E_a}{2.303R}$$

$$E_a = -2.303R \times \text{slope}$$

- Alternatively, let k_1 and k_2 are the rate constants for the reaction at two different temperatures T_1 and T_2 respectively.

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1}$$

$$\log k_2 = \log A - \frac{E_a}{2.303RT_2}; \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

By solving this, one can calculate activation energy.

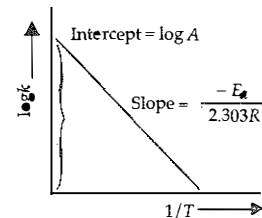


Illustration 5

For a reaction, specific rate constant at 283 K is $2.25 \times 10^{-6} \text{ L mol}^{-1} \text{ sec}^{-1}$ and at 293 K is $2.5 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$. Compute the energy of activation of the reaction.

Soln.: From Arrhenius equation

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

$$\text{or, } E_a = \frac{2.303R \times T_1 \times T_2}{(T_2 - T_1)} \times \log \frac{k_2}{k_1}$$

$$= \frac{2.303 \times 8.31 \times 283 \times 293}{10} \times \log \frac{2.50 \times 10^{-5}}{2.25 \times 10^{-6}}$$

$$= 165951.0489 \text{ J} = 165.94 \text{ kJ mol}^{-1}$$

Illustration 6

The activation energy of a non-catalysed reaction at 37°C is 20.0 kcal mol⁻¹ and activation energy of the same reaction catalysed by a transition metal is 6.0 kcal mol⁻¹, compute the ratio of rate constants of the catalysed and non-catalysed reactions.

Soln.: We know that $k = Ae^{-E_a/RT}$

Let k_2 and k_1 be the rate constants of catalysed and non-catalysed reactions respectively. Assuming Arrhenius pre-exponential factor A to be same in both cases

$$\frac{k_2}{k_1} = \frac{e^{-E_a/RT} \text{ (catalysed)}}{e^{-E_a/RT} \text{ (non-catalysed)}} = e^{\frac{E_{a1} - E_{a2}}{RT}} = e^{\left[\frac{20-6}{RT} \right]}$$

$$= e^{\left[\frac{(14) \times 1000}{2 \times 310} \right]} = e^{22.58}$$

$$\log_e \frac{k_2}{k_1} = 22.58 \text{ or } 2.303 \log \frac{k_2}{k_1} = 22.58$$

$$\log \frac{k_2}{k_1} = \frac{22.58}{2.303} = 10;$$

$$\therefore k_2/k_1 = \text{antilog } 10 \Rightarrow \frac{k_2}{k_1} = 10^{10}$$