

CLASS - B.Sc (Hons) PART - III

PAPER - V

TOPIC - Arrhenius equation

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Q Describe Arrhenius equation showing the influence of temperature on reaction rates.

Ans. In 1889 Arrhenius proposed that the temperature dependence of reaction rates can be obtained from Van't Hoff's reaction isochore -

$$\frac{d(\ln K_c)}{dT} = \frac{\Delta E}{RT^2} \quad \text{--- (1)}$$

where $\Delta E = E_p - E_r$. E_p and E_r are the energy of product and reactant respectively. K_f and K_r are the rate constants for forward and reverse reactions respectively. Then

$$K_c = \frac{K_f}{K_r}$$

$$\therefore \frac{d \ln K_f}{dT} - \frac{d \ln K_r}{dT} = \frac{E_p - E_r}{RT^2}$$

But $E_p - E_r = E_{a(f)} - E_{a(r)}$ where $E_{a(f)}$ and $E_{a(r)}$ are the activation energy for the forward and reverse reactions respectively.

$$\therefore \frac{d \ln K_f}{dT} - \frac{d \ln K_r}{dT} = \frac{E_{a(f)}}{RT^2} - \frac{E_{a(r)}}{RT^2} \quad \text{--- (2)}$$

Equation (2) can be shown as

$$\frac{d \ln K_f}{dT} = \frac{E_{a(f)}}{RT^2} + \text{Constant}$$

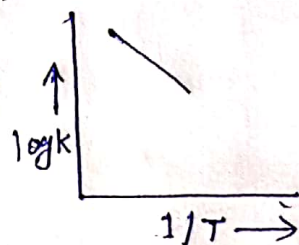
$$\frac{d \ln K_r}{dT} = \frac{E_{a(r)}}{RT^2} + \text{Constant}$$

Experimentally, it was found that the constant can be set to zero, which provides the relationship between the rate constant (k) and temperature (T) as -

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \text{or} \quad d \ln k = \frac{E_a}{R} \cdot \frac{dT}{T^2} \quad \text{--- (3)}$$

Since the constant is actually zero, hence any reaction path from reactants to products has two directions. Common observation that one of the two directions is more favoured shows the presence of an intermediate state or energy barrier having energy greater than either of the two. This leads to the idea of an activated state. The amount of energy in excess to the average energy possessed by the reactant molecules to form the activated state is called activation energy. Hence only those reactant molecules having energy equal to or greater than activation energy would be able to form products.

Therefore the rate of reaction is determined by activation energy. The fast and slow reactions have low and high activation



energies respectively. If $E_a(f) < E_a(r)$ then the reaction is exothermic and if $E_a(f) > E_a(r)$, then the reaction is endothermic. On integration, the equation (3) gives

$$\ln k = \frac{-E_a}{RT} + \ln A$$

where A is the integration constant.

$$\left[\begin{array}{l} \therefore \int x^n dx = \frac{x^{n+1}}{n+1} + C \\ \therefore \int T^{-2} dT = \frac{T^{-2+1}}{-2+1} = \frac{T^{-1}}{-1} \\ \qquad \qquad \qquad = \frac{1}{T} \end{array} \right]$$

$$\text{or } \log k = \frac{-E_a}{2.303R} \cdot \frac{1}{T} + \log A \quad \dots (4)$$

$$\Rightarrow k = Ae^{-E_a/RT} \quad \dots (5)$$

This is called Arrhenius relation and A is called frequency factor. Thus the E_a cannot be measured directly but can be evaluated. If $\log k$ is plotted against $1/T$, a straight line would be obtained with the slope = $\frac{-E_a}{2.303}$, from which E_a can be evaluated. Alternatively by integrating equation (3) between the limits T_1 & T_2 when the corresponding values of k are k_1 & k_2 respectively, we get -

$$\int_{k_1}^{k_2} d \ln k = \int_{T_1}^{T_2} \frac{E_a}{RT^2} dT = \frac{E_a}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

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

Thus by measuring the rate constants k_1 and k_2 at two different temperatures T_1 & T_2 respectively. We can calculate E_a . When E_a is known, A can be calculated.

This equation shows the temperature dependence of rate constant in terms of E_a and A which are characteristic of the reaction. A & E_a are assumed to be constant over the small range of temperatures.