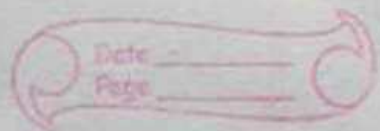


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For Deg III Chem Hons, Session 2020-2021

Topic :- Chemical Kinetics, Paper-V

Arrhenius equation: -

Van't Hoff proved that the value of equilibrium constant varied with the temperature. On the basis of this, Van't Hoff suggested that the logarithm of the rate constant of a chemical reaction must be a linear function of the reciprocal of the absolute temperature.

Arrhenius extended the above suggestion of Van't Hoff and gave his own hypothesis. According to him -

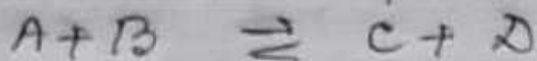
- (1) All the molecules of a system cannot take part in the chemical reaction.
 - (2) It is only a certain number of molecules which react. These reacting molecules are known as active molecules.
 - (3) The molecules which do not take part in a chemical reaction are known as ~~inert~~ Passive molecules.
 - (4) There exists an equilibrium between Passive and active molecules¹
- $$M(\text{Passive}) \rightleftharpoons M(\text{Active})$$

(5) When the temperature is raised, the equilibrium between active and passive molecules shifts towards the right. This increases the number of active molecules which are ready to take part in a reaction. Thus, the increase in reaction rate with rise in temperature is due to the increase in the number of active molecules than due to the number of collisions.

"Thus the Passive molecules can become activated by absorption of heat energy

Derivation of Arrhenius equation

Consider the following reversible equation



Rate of forward reaction = $k_1 [A] \cdot [B]$

Rate of backward reaction = $k_2 [C] \cdot [D]$

At chemical equilibrium

$$k_1 [A] \cdot [B] = k_2 [C] \cdot [D]$$

$$\text{or } \frac{k_1}{k_2} = \frac{[C] \cdot [D]}{[A] \cdot [B]}$$

$$\text{or } K_c = \frac{[C] \cdot [D]}{[A] \cdot [B]} \quad \text{where } K_c = \text{Equilibrium Constant} = \frac{k_1}{k_2} \quad \text{--- (1)}$$

From Thermodynamics, Van't Hoff equation is

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

substituting the value of $K_c = K_1/K_2$ in eq (II)

$$\frac{d \log \frac{K_1}{K_2}}{dT} = \frac{\Delta E}{RT^2} \quad \text{--- (III)}$$

$$\text{or } \frac{d \log K_1}{dT} - \frac{d \log K_2}{dT} = \frac{\Delta E}{RT^2}$$

Van't Hoff Proposed that equation (III) can be split up into two equations as follows -

$$\frac{d \log K_1}{dT} = \frac{E_1}{RT^2} + I \quad \text{--- (IV)}$$

$$\frac{d \log K_2}{dT} = \frac{E_2}{RT^2} + I \quad \text{--- (V)}$$

Where $\Delta E = E_1 - E_2$ and I is constant. It was observed that I was independent of temperature. Therefore I must be equal to zero in equation (IV) and (V) hence

$$\frac{d \log K_1}{dT} = \frac{E_1}{RT^2} \quad \text{--- (VI)}$$

$$\frac{d \log K_2}{dT} = \frac{E_2}{RT^2} \quad \text{--- (VII)}$$

Equation (VI) and (VII) are known as Arrhenius equation.

Integrating equation (VI) and (VII) we get

$$\log K_1 = -\frac{E_1}{RT} + \text{Constant } A \quad \text{--- (VIII)}$$

$$\log K_2 = -\frac{E_2}{RT} + \text{Constant } A \quad \text{--- (IX)}$$

Equation (VIII) and (IX) can be put as

$$K_1 = Ae^{-E_1/RT}$$

$$K_2 = Ae^{-E_2/RT}$$

$$\text{In general } K = Ae^{-E/RT} \quad \text{--- (X)}$$

In equation (X) A is a constant. It is generally known as frequency factor of the reaction. E is a term which has the dimension of Energy and is known as energy of activation. Equation (X) is known as integrated form of Arrhenius equation. This equation expresses the dependence of K in terms of A and E. Both A and E are characteristics of the reaction.

Indy

Determination of A and E

The logarithmic form of equation (X) is

$$\log K = \log A - \frac{E}{RT}$$

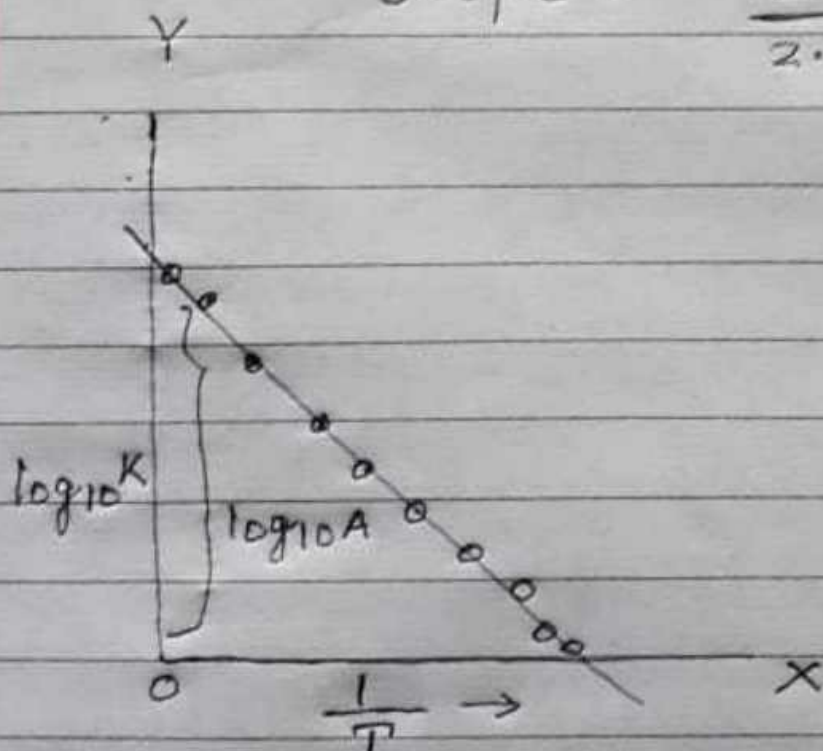
or since it is more convenient to use $\log_{10}$

$$\log_{10} K = \log_{10} A - \frac{E}{2.303 RT}$$

If $\log_{10} K$ is plotted against $\frac{1}{T}$, a straight line will be obtained.

The slope of this line is

$$\text{slope} = \frac{-E}{2.303 R}$$



Thus knowing the slope, the value of E can be easily calculated. The ~~intercept~~ intercept of the line on y-axis will give the value of $\log_{10} A$.

Such a plot is shown above in figure.