UNIT-11 : CHEMICAL KINETICS [JEE – MAIN CRASH COURSE]

Rate of Reaction

Rate of reaction is defined as the rate of change in concentration of either reactants or products per mole.

$$A \rightarrow B$$

$$R_{\text{av}} = \frac{-\Delta n_A}{\Delta t};\ R'_{\text{av}} = \frac{\Delta n_B}{\Delta t};\ R_{\text{av}} = R'_{\text{av}}$$

Instantaneous Rate of Change of the Amount of a Reactant and a Product

$$R_{\text{ins}} = \lim_{\Delta t \to 0}\left(\frac{-\Delta n_A}{\Delta t}\right) = -\frac{dn_A}{dt} \text{ or } R_{\text{ins}} = \lim_{\Delta t \to 0}\left(\frac{\Delta n_B}{\Delta t}\right) = \frac{dn_B}{dt}$$

Order of a Reaction

For a general reaction: $aA + bB \rightarrow cC + dD$.

$$r = k[A]^{a'}[B]^{b'}$$

where the dimensionless exponents a' and b' may or may not be equal to a and b, respectively. The constants a' and b' may have positive, negative integral or fractional values or zero value. The constant a' is known as the order of the reaction with respect to A, b' as the order of the reaction with respect to B, and so on. The sum $(a' + b')$ is known as the overall order of the reaction.

It may be emphasized once again here that the rate equation with its rate constant and order of various reacting species is an experimental finding and cannot be predicted from the stoichiometry of the balanced reaction.

Integrated Rate Law of First-Order Reaction

If the reaction $aA + bB \rightarrow$ products is first order with respect to A and zero order with respect to B, we have

$$r = -\frac{1}{a}\frac{d[A]}{dt} = k[A] \text{ or } -\frac{d[A]}{dt} = ak[A]$$

On integrating, we get

$$\ln\left(\frac{[A]_0}{[A]_0 - ax}\right) = akt$$

Characteristics of First-Order Reactions

$$\ln[A]_0 - \ln([A]_0 - x) = kt$$

$$\log([A]_0 - x) = \log[A]_0 - \frac{kt}{2.303}$$

It may also be written as $[A]t = [A]_0\, e^{-kt}$.

The equation, which is known as Wilhelmy's equation, indicates that the concentration of A decreases exponentially with time. The decrease is such that the time required for a definite fraction of the reaction to occur is independent of the initial concentration of the reactant.

Half Life of a Reaction

Half life, $t_{1/2}$, of a reaction is the time required for the concentration of the reactant to decrease by half, i.e., $[A]_t = \frac{1}{2}[A]_0$

$$t_{1/2} = \frac{0.693}{k}$$

This relation indicates that $t_{1/2}$ is independent of initial concentration.

Half Life of a *n*th Order Reaction

$$A \rightarrow \text{Product}$$

$$-\frac{d[A]}{dt} = k_n [A]^n$$

$$\frac{(1-2^{n-1})}{(1-n)[a]_0^{n-1}} = k_n t_{1/2}$$

$$t_{1/2} = \frac{(2^{n-1}-1)}{(n-1)[A]_0^{n-1} k_n}$$

$$\therefore \quad t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

Concentrations Replaced by Other Quantities in First-Order Integrated Rate Law

Case I: Let there be a first-order reaction of the type $A \rightarrow B + C$. Let us assume that all the three species are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	T	∞
Partial pressure of A	P_0	P_t	–

Rate constant for this case is given as

$$k = \frac{1}{t} \ln \frac{A_0}{A_t}$$

$$= \frac{1}{t} \ln \frac{P_0}{P_t}$$

Case II:

$$A_{(g)} \rightarrow B_{(g)} + C_{(g)}$$

Time	0	T	∞
Partial pressure of $A + B + C$	–	P_t	P_∞

Rate constant for this case is given as

$$k = \frac{1}{t} \ln \frac{P_\infty}{2(P_\infty - P_t)}$$

Case III: Now, let us assume a first-order reaction $A \rightarrow B + C$ such that A, B, and C are in solution. At time zero, a small amount of the solution is taken, cooled (to stop the reaction from proceeding), and titrated with a suitable reagent. Let us assume that the reagent reacts only with A and not with B and C. The same process is repeated at time t.

Time	0	t
Volume of reagent	V_0	V_t

Rate constant for this case is given as

$$k = \frac{1}{t} \ln \frac{V_0}{V_t}$$

Case IV: Now, let us assume that A, B, and C are optically active compounds, which rotate the plane polarized light in the clockwise or anticlockwise direction.

$$A(\text{soln.}) \rightarrow B(\text{soln.}) + C(\text{soln.})$$

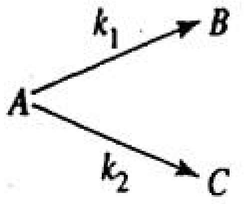
Time	0	t	∞
Total rotation in degrees	r_0	r_t	r_∞

Rate constant for this case is given as

$$k = \frac{1}{t}\ln\frac{r_\infty - r_0}{r_\infty - r_t}$$

Parallel (or Simultaneous) Reactions

Reactions in which two products are formed from same set of reactant(s) by different paths are called parallel or simultaneous reactions.



$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A]$$

$$\frac{d[B]}{dt} = k_1[A]; \quad \frac{d[C]}{dt} = k_1[A]$$

$$\ln\frac{[A_0]}{[A_t]} = (k_1 + k_2)t$$

$$\frac{(d[B]/dt)}{(d[c]/dt)} = \frac{k_1}{k_2}$$

$$\therefore \quad \frac{x}{y} = \frac{k_1}{k_2}$$

Effect of Temperature on Reactions Rate

Temperature coefficient is the ratio of rate constants of a chemical reaction at two temperatures differing by 10°C. The value of temperature coefficient for most of the reactions lies between two and three. Therefore,

$$\text{Temperature coefficient} = \frac{k_{T+10}}{k_T} \approx 2 \text{ to } 3$$

The actual dependence of rate constant on temperature is represented by the Arrhenius equation,

$$k = Ae^{-E_a/RT}.$$

Interpretation of Arrhenius Equation

Arrhenius equation represents the dependence of the rate constant k of a reaction on the absolute temperature T:

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

where the factor $e^{-E_a/RT}$ refers to the fraction of collisions (also effective collisions) that have the sufficient activation energy to collide and form products and A is the number of effective collision per unit time. Therefore, the product of A and $e^{-E_a/RT}$ is the number of collisions that actually lead to the formation of products.

Determination of activation energy

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

where k_1 and k_2 are rate constants at temperatures T_1 and T_2 kelvin, respectively. Knowing these values, E_a can be calculated. Care must be taken to insert the value of R in a unit in which E_a is desired.

Main characteristics of arrhenius equation

- The larger the activation energy of a reaction, the smaller is the value of rate constant.
- The larger the activation energy of a reaction, the greater is the influence of change in temperature on rate constant.
- For lower temperature range, increase in temperature causes more change in the value of k than the same increase in temperature of high temperature range.

Radioactivity

All radioactive decay follows first-order kinetics. The only difference from chemical reactions is that temperature does not influence the rate of radioactive decay.

$$A \rightarrow B$$

$$\frac{-dN_A}{dt}=\lambda N_A; \quad \ln\frac{N_0}{N_t}=\lambda t; \quad N_t=N_0\, e^{-\lambda t}$$

$$t_{1/2}=\frac{0.693}{\lambda}; \quad t_{\text{av}}=\frac{1}{\lambda}$$

- Activity of a radioactive element is the rate at which it decays and is given by λN.
- Specific activity is the activity of a unit mass of a radioactive substance.

SOME IMPORTANT EXAMPLES

Example 1 The half life of first-order decomposition of NH_4NO_3 is 2.10 h at 288 K temperature: $NH_4NO_{3(aq)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}$. If 6.2 g of NH_4NO_3 is allowed to decompose, the time required for NH_4NO_3 to decompose 90% and the volume of dry N_2O produced at this point measured at STP are, respectively:

(a) 6.978 h, 2.016 L
(b) 0.319 h, 2.12 L
(c) 0.319 h, 2.016 L
(d) None of these

Solution (a)

$$k = \frac{0.693}{2.1} = 0.33\,\text{h}^{-1}$$

Let t be the time for 90% decomposition. So

$$a = 100\% \; x = 90 \text{ or } (a-x) = 10$$

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$\Rightarrow \qquad t = \frac{2.303}{0.33}\log\left(\frac{100}{10}\right); t = 6.978\,\text{hr}$$

$$n_{NH_4NO_3} \text{ taken} = \frac{6.2}{62} = 0.1$$

As per question,

$$\text{Number of moles of } N_2O \text{ produced} = 0.1 \times \frac{90}{100}$$

$$\text{Volume of } N_2O \text{ produced at STP} = 0.09 \times 22.4 = 2.016\text{ L}$$

Example 2 A fresh radioactive mixture contains short lived species A and B. Both emitting α-particles initially at 8000 α-particles per minute. After 20 min, they emit at the rate of 3500 α-particles per minute. If the half lives of the species A and B are 10 min and 500 h, respectively, then the ratio of activities of $A : B$ in the initial mixture was:

(a) 4 : 6 (b) 6 : 4 (c) 3 : 4 (d) 3 : 1

Solution (d)

Let initial activities of A and B are A_0 and B_0

($\because$ after 2 half lives of activity of A will remain $\frac{A_0}{4}$)

$$A_0 + B_0 = 8000 \text{ and also } \frac{A_0}{4} + B_0 = 3500$$

We can assume that activity of B remains constant due to larger half life. So

$$\frac{3A_0}{4} = 4500; A_0 = 6000; B_0 = 2000; \; \frac{A_0}{B_0} = \frac{6000}{2000} = \frac{3}{1}$$

Example 3 The decomposition of a gaseous substance (A) to yield gaseous products (B) and (C) follows first-order kinetics. If initially only (A) is present and 10 min after the start of the reaction the pressure of (A) is 200 mm Hg and that of overall mixture is 300 mm Hg, then the rate constant for $2A \rightarrow B + 3C$ is:

(a) (1/600) ln 1.25 s^{-1} (b) (2.303/10) log 1.5 min^{-1}

(c) (1/10) ln 1.25 s^{-1} (b) None of these

Solution (a)

$$\begin{array}{lcccc} & 2A & \rightarrow B & + & 3C \\ t=0 & P_0 & 0 & & 0 \\ t=t & P_0-P' & P' & & 3P' \\ t=t_\infty & 0 & P_0/2 & & 3P^\circ/2 \end{array}$$

Given $P_0 - 2P' = 200$

$P_0 + 2P' = 300$

So, $2P_0 = 500$ and $P' = 25$

$$k = \frac{2.303}{t}\log\left(\frac{250}{200}\right)$$

$$k = \frac{2.303}{10}\log 1.25$$

$$k = \frac{1}{600}\ln(1.25)\sec^{-1}$$

Example 4 The reaction $A_{(s)} \rightarrow 2B_{(g)} + C_{(g)}$ is first order. The pressures after 20 min and after very long time are 150 mm Hg and 225 mm Hg, respectively. The value of rate constant and pressure after 40 min are:

(a) 0.05 ln 1.5 min^{-1}, 200 mm Hg (b) 0.5 ln 2 min^{-1}, 300 mm Hg

(c) 0.05 ln 3 min^{-1}, 300 mm Hg (d) 0.05 ln 3 min^{-1}, 200 mm Hg

Solution (d)

$$A_{(s)} \rightarrow 2B_{(g)} + C$$

$$K = \frac{1}{t}\ln\left(\frac{P_\infty - P_0}{P_\infty - P_t}\right) \qquad P_0 = 0$$

$P_t = 150$ $\qquad$ $P_\infty = 225$

$$k = \frac{1}{20}\ln\left[\frac{225}{225-150}\right]$$

$$= \frac{1}{20}\ln\left(\frac{225}{75}\right) = 0.05\ln 3$$

$$\frac{1}{20}\ln\left(\frac{225}{75}\right) = \frac{1}{20}\ln\left(\frac{225}{225\times P_{40}}\right)$$

$$\Rightarrow \qquad \left(\frac{225}{75}\right)^2 = \frac{225}{225\times P_{40}}$$

$$\frac{225}{75\times 75} = \frac{1}{225-P_{40}} \quad \Rightarrow \quad P_{40} = 200$$

Example 5 The time elapsed for a certain reaction between 33% and 67% completion of a first-order reaction is 30 min. What is the time needed for 25% completion?

(a) 150.5 min (b) 12.5 min (c) 180.5 min (d) 165.5 min

Solution **(b)**

$$t_1 = \frac{2.303}{k}\log\left(\frac{100}{67}\right)$$

$$t_2 = \frac{2.303}{k}\log\left(\frac{100}{33}\right)$$

$$(t_2 - t_1) = \frac{2.303}{k}\left[\log\frac{100}{33}\times\frac{67}{100}\right]$$

$$(t_2 - t_1) = \frac{2.303}{k}\times 0.30 = 30$$

$$k = \frac{2.303}{30}\times\frac{30}{100} = 2.303\times 10^{2}$$

$$t = \frac{2.303}{2.303\times 10^{-2}}\log\left(\frac{100}{75}\right)$$

$$= 100\,[\log 4 - \log 3]$$

$$= 100[.6020 \times 0.4771]$$

$$= 12.49 = 12.5 \text{ min}$$