Chapter 4

CHEMICAL KINETICS

The branch of physical chemistry which deals with the study of rate of reaction and their mechanism is called chemical kinetics.

❖ RATE OF REACTION

Consider a hypothetical reaction-

$$R \rightarrow P$$

If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

$$\Delta t = t_2 - t_1$$

Change in concentration of reactant, $\Delta[R] = [R]_2 - [R]_1$

Change in concentration of Product, $\Delta [P] = [P]_2 - [P]_1$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R = Decrease in concentration of R / Time taken

$$= -\frac{\Delta[R]}{\Delta t} \qquad \text{................(4.1)}$$

Rate of appearance of P = Increase in concentration of P / Time taken

$$= \frac{\Delta[P]}{\Delta t} \qquad \text{..................(4.2)}$$

Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –

to make the rate of the reaction a positive quantity.

For a general assumed reaction of type-

$$mA + nB \longrightarrow pC + qD$$

where m n p and q are stoichiometry coefficient .the rate of reaction may given as-

$$\frac{-\Delta[A]}{m\Delta t} = -\frac{\Delta[B]}{n\Delta t} = \frac{\Delta[C]}{p\Delta t} = \frac{\Delta[D]}{q\Delta t} \qquad \text{................. (4.3)}$$

The rate we have studied is called ***average rate of reaction***.

Rate at particular instance is called instantaneous rate for inst t→0 means it tends to be zero.

$$\text{Instantaneous rate } r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{t} \qquad \ldots\ldots\ldots\ldots\ldots (4.4)$$

More accurate difference between inst rate and avg rate may understood from graph [fig: 4.1] given below-

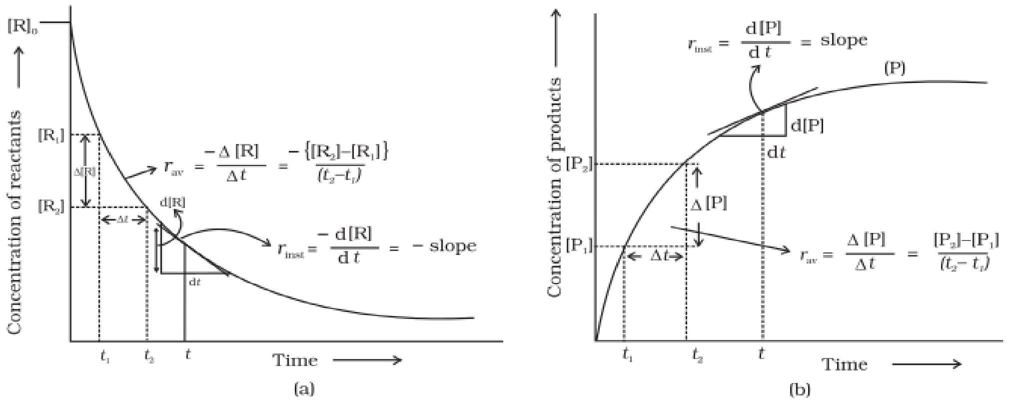


Fig. 4.1: Instantaneous and average rate of a reaction

Units of rate of a reaction

a. time^{-1}.
b. For example, if concentration is in mol L^{-1} and time is in seconds then the units will be mol L^{-1}s^{-1}.
c. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s^{-1}.

❖ Factors affecting rate of reaction-

- Temperature [see later]
- Catalyst [see later]
- Concentration[see in rate law]

❖ Rate Law-

Generally rate of reaction is directly proportional to c

For a reaction $mA \longrightarrow$ Product,

rate may given as

$$\underline{R = k\,[A]^{m}}$$

For a reaction $xA + yB \longrightarrow$ Product

rate of reaction may given as-

$$\underline{Rate = k\,[A]^{x}\,[B]^{y}}$$

However it must be noted that x and y are practically determined values which may or may not equal to reaction coefficient. Hence rate law may defined as-

- *rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometry coefficient of the reacting species in a balanced chemical equation*
- Unit of rate constt may given as-

$$k = \frac{unit\ of\ rate}{unit\ of\ concentration}$$

Order of reaction

- In the rate equation

  $$\text{Rate} = k\,[A]^x\,[B]^y$$

  x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.
- Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.
- Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.
- For Example **:** Calculate the overall order of a reaction which has the rate expression

  (a) $\text{Rate} = k\,[A]^{1/2}\,[B]^{3/2}$

  (b) $\text{Rate} = k\,[A]^{3/2}\,[B]^{-1}$

  As we know that if $\text{Rate} = k\,[A]^x\,[B]^y$ then order of reaction $= x + y$

  So order for (a) $1/2 + 3/2 = 2$, i.e., second order

  for (b) $3/2 + (-1) = 1/2$, i.e., half order.

Moleculart of reaction

- The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called Moleculart of a reaction.
- The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

  $$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

- Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

  $$2HI \rightarrow H_2 + I_2$$

- Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

  $2NO + O_2 \rightarrow 2NO_2$
- The probability that more than three molecules can collide and react simultaneously is very small. Hence, the Moleculart greater than three is not observed.

Zero Order Reactions

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$

$$\text{Rate} = -d[R]/dt = k[R]^{\circ}$$

As any quantity raised to power zero is unity

$$\text{Rate} = -d[R]/dt = k \times 1$$

$$d[R] = -k\,dt$$

Integrating both sides

$$[R] = -kt + I \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.5)$$

where, I is the constant of integration.

At t = 0, the concentration of the reactant R = $[R]_0$, where $[R]_0$ is initial concentration of the reactant. Substituting in equation…………….. (4.5)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (4.5)

$$[R] = -kt + [R]_0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.6)$$

Comparing (4.6) with equation of a straight line, y = mx + c, if we plot [R] against t, we get a straight line (Fig. 4.3) with slope = –k and intercept equal to $[R]_0$.

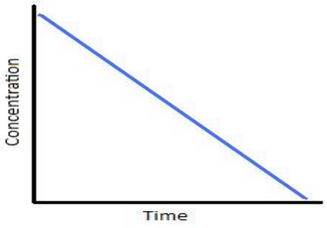
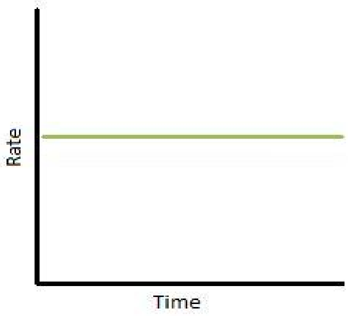


Fig:4.3 graph of eq 4.6



This graph shows that zero order reaction does not depends on concentration of reactant

Further simplifying equation (4.6), we get the rate constant, k as

$$k = \frac{[R]-[R]_0}{t} \qquad \text{……………………………….(4.7)}$$

The above equation is characteristic of zero order kinetics.

Some enzyme catalyzed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

$$2NH_3\ g \quad \overset{1130K}{\text{Pt catalyst}} \quad N_2\ g + 3H_2\ g$$

$$\text{Rate} = k\,[NH_3]^0 = k$$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero order reaction.

❖ <u>First Order reaction</u>

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k\,[R]$$

$$\text{Or} \qquad \frac{d[R]}{[R]} = -\,kdt$$

Integrating this equation, we get

$$\ln[R] = -kt + I \text{…………………………(4.8)}$$

Again, I is the constant of integration and its value can be determined easily.

When t = 0, R = $[R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (4.8) can be written as

$$\ln[R]_0 = -k \times 0 + I$$

$$\ln[R]_0 = I$$

Substituting the value of I in equation (4.8)

$$\ln[R] = -kt + \ln[R]_0 \qquad \text{…………………(4.9)}$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

or $$-k = \frac{1}{t} \ln \frac{[R]}{[R]_0} \qquad \text{…………………(4.10)}$$

Or $$k = -\frac{1}{t} \ln \frac{[R]}{[R]_0}$$

Or $$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \qquad \text{…………………..(4.11)}$$

Where,

k= first order rate constt.

$[R]_0$ = initial concentration

$[R]$ = concentration after ‘t’ time

If we plot a graph between log $[R]_0/[R]$ vs. t, (Fig. 4.5 and 4.6), the slope = k/2.303 and the intercept be $\ln[R]_0$

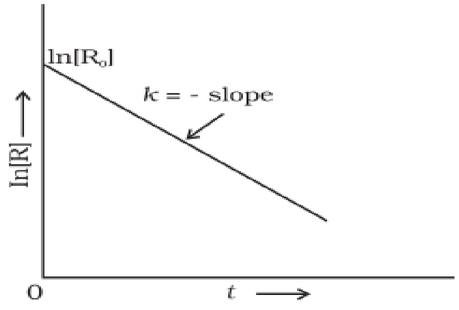


Fig. 4.4: A plot between ln[R] and t for a first order reaction

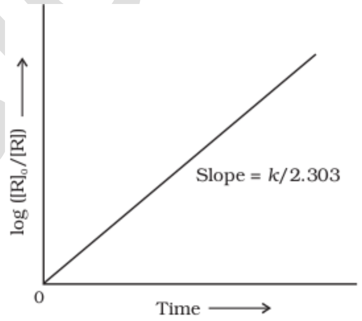


Fig. 4.5: Plot of log $[R]_0/[R]$ vs time for a first order reaction

❖ Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.
For a zero order reaction, rate constant is given by equation (4.7)

$$k = \frac{[R]-[R]_0}{t}$$

At $t = t_{1/2}$, Then $[R] = \frac{[R]_0}{2}$

Putting these values in above equation and on solving we get-

$$t_{1/2} = \frac{[R]_0}{2k} \qquad \text{……. ……(4.12)}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,

the rate constt for first order reaction is given by equation (4.11) as

$$k = \frac{2.303}{t} \log\frac{[R]_0}{[R]}$$

for half life t is assumed to be $t_{t/2}$ and [R] be $[R]_0$. On putting these values in above equation and solving we get-

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

$$k = \frac{2.303}{t_{1/2}} \log 2$$

$$k = \frac{2.303}{t_{1/2}} \times 0.3010$$

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

$$t_{1/2} = \frac{0.693}{k} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.13)$$

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{1/2} \propto [R]_0$. *For first order reaction* $t_{1/2}$ *is independent of* $[R]_0$.

Q.A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half-life of the reaction.

❖ Temperature Depndence of the rate of a reaction/Arhenius Equation

- It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.
- If rate constt at t emperature is k_t and at t=10 is $k_{t=10}$ then new rate constt may calculated as

$$K = \frac{k_{t+10}}{k_t} \qquad \ldots\ldots\ldots\ldots\ldots\ldots..(4.14)$$

- The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.
- It was first proposed by Dutch chemist, J.H. Van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation .

$$k = A\, e^{-Ea / RT} \qquad \text{………………}(4.15)$$

where A is the Arrhenius factor or frequency factor or pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and Ea is activation energy measured in joules/mole (J mol $^{-1}$).

Taking natural log to both side

$$\ln k = \ln(Ae^{-Ea /RT})$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{………}(4.16)$$

If we plot graph between ln k vs. 1/T the slope be a straight line as represented in graph 4.10. the intercept will be the value of in A.

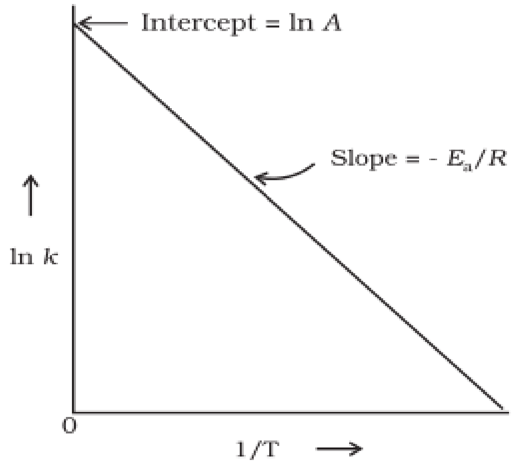


Fig. 4.10: A plot between ln k and 1/T

Returning back to equation 4.16, by replacing antilog by log we have-

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

$$\log k = \log A - \frac{E_a}{2.303RT} \qquad \text{…………}(4.17)$$

The equation 4.16 is broadly used in calculation.

Now assume that k_1 and k_2 are rate constt at t_1 and t_2 respectively then equation can written for k_1 and k_2 as-

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

$$\log k_2 = \log A - \frac{E_a}{2.303RT_2}$$

On subtracting we have- $$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \text{…………}(4.18)$$

Equation Eq 4.17 is also used in solving numerical problems.

❖ Effect of Catalyst

A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change. For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.

$$2KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$$

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 temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. 4.11.

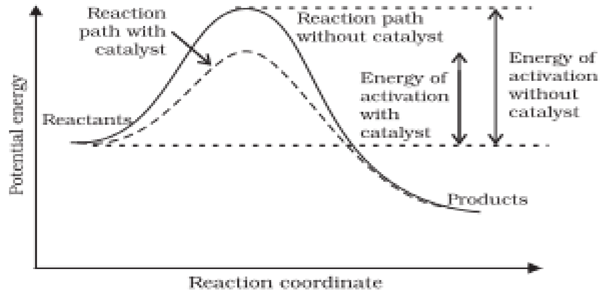


Fig. 4.11: Effect of catalyst on activation energy

It is clear from Arrhenius equation (4.18) that lower the value of activation energy faster will be the rate of a reaction.

Problems-

1. NCERT book question [find in book]

2. NCERT Exemplar problems [included]