Chapter 2

Chemical Kinetics Lecture/Lession Plan -1

Chemical Kinetics

2.1 Concept of chemical kinetics

Chemical kinetics deals with the rate of a chemical reaction, mechanism of a chemical reaction and external effects like temperature, pressure, catalyst etc on the rate of a chemical reaction. The rate of a chemical reaction indicates that with time the rate of formation of product or with time the rate of disappearance of reactant.

2.2 On the basis of speed chemical reactions are three types-

1) Instantaneous reaction
2) Moderate reaction
3) Very slow reaction.

1) Instantaneous reaction: Those reactions which occur in very very short period of time (say 10^{-13} to 10^{-16}sec) is called instantaneous reaction. Any ionic reactions are the example of instantaneous reaction.

$$AgNO_3 + NaCl \rightarrow AgCl \downarrow + Na^+ + NO_3^-$$

2) Moderate reaction: Those reactions which occur in not so fast or not so slow that is moderate period of time say some minutes to some hours is called moderate reaction. Examples are-

$$\text{a)}\ H_2O_2 \rightarrow H_2O + O_2$$
$$\text{b)}\ CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

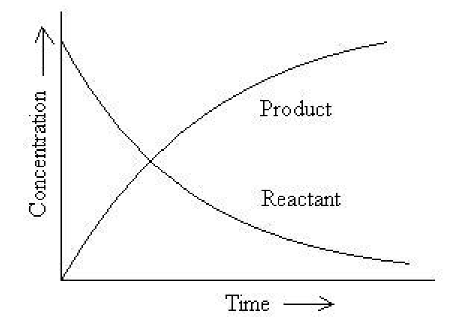
3) Very slow reaction These reaction occur with a long period of time, say some years to few years is called very slow reaction. Examples are- rusting of iron

$$Fe + H_2O_2 + CO_2 + \frac{1}{2}O_2 \rightarrow Fe(OH)HCO_3$$

2.3 Chemical reaction are mainly two types-

1) One directional reaction
2) Reversible reaction
1) One directional reaction: There are some reactions which occur in one direction; that means reactant converted into product only. In thitype of reaction the concentration of the reactants gradually decreases with time and the concentration of the product increase with time and after certain time there will be no reactant in the reaction chamber. Decomposition of $CaCO_3$ into CaO and CO_2 in an open vassel is an example of one directional reaction.

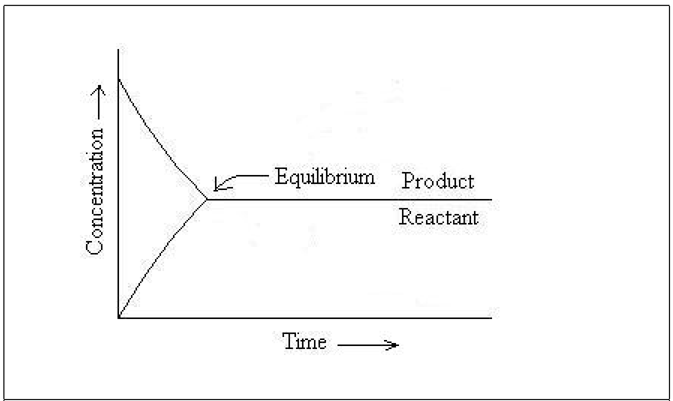
$$CaCO_3 + \text{Heat} \rightarrow CaO + CO_2 \uparrow \text{(in a open vassel)}$$



reaction rate change with time for one direction reaction

2) Reversible reaction: There are some reactions which occur in both direction; that means reactant converted to product and after certain time product converted to reactant back. At that time the rate of change in concentration of the reactant will equal to the rate of change in concentration of the product. In this reaction the concentration of the reactants and product does not change with time but both forward and backward reaction occurs in same rate. In this state the reaction is called equilibrium reaction. So equilibrium reaction is dynamic in nature and not static. If the above chemical reaction occur in a close vessel, then it will follow a reversible pathway.

$$CaCO_3 + \text{Heat} \rightarrow CaO + CO_2 \uparrow \text{(in a close vassel)}$$



reaction rate change with time for reversible reaction

2.4 Rate

Thus rate of a chemical reaction is the ratio of change of concentration (Δc) of either reactant or product with time (Δt).

$$\text{Rate} = \frac{\text{change in concentration } (\Delta c)}{\text{change in time } (\Delta t)}$$

So, the rate of reaction can be defined as increased in concentration of product per unit time or decrease in concentration of reactant per unit time. Hence when we express a reaction rate with respect to change of concentration of product, we will use a positive sign as concentration is increasing for product and similarly we will use negative sign for a rate expression with respect to reactants as the concentration of the reactants decrees with time.

$$\text{Rate} = (-)\frac{\text{change in concentration of reactant } (\Delta c_R)}{\text{change in time } (\Delta t)}$$

$$\text{Rate} = (+)\frac{\text{change in concentration of product } (\Delta c_P)}{\text{change in time } (\Delta t)}$$

2.4.1 Unit of rate of a reaction:

Unit of rate of a reaction will be the ratio of unit of concentration with unit of time.

$$\begin{aligned}\text{Thus, unit of rate of reaction} &= \frac{\text{unit of concentration}}{\text{unit of time}} \\ &= \frac{\text{mol.lit}^{-1}}{\text{sec}} \\ &= \text{mol.lit}^{-1}.\text{sec}^{-1}\end{aligned}$$

The rate of a chemical reaction depends upon this following factors-
i) **Concentration:** Generally reaction rate increases with increasing concentration of reactants.

ii) **Temperature:** For a homogeneous reaction rate of a reaction increases twice to thrice with every 10^{o}C increase of temperature.
iii) **Catalyst:** Presence of catalyst can control the rate of a reaction significantly.
iv) **Substrate:** Generally rate of ionic substrates are fast compared to covalent substrate.
v) **Surface area:** For solid substrate, rate of reaction increases with increase in surface area of reactants.

2.5 Relation of rate with stoichiometry

Let us consider a chemical reaction with following balanced equation-

$$\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3}$$

So, two molecules of ammonia is formed from one molecule of nitrogen and three molecule of hydrogen. From this chemical equation we can say that consumption of hydrogen is three times of nitrogen-

$$\frac{d[\mathrm{H_2}]}{dt} = 3\frac{d[\mathrm{N_2}]}{dt}$$
$$\frac{1}{3}\frac{d[\mathrm{H_2}]}{dt} = \frac{d[\mathrm{N_2}]}{dt}$$

Now as both nitrogen and hydrogen are reactants in this reaction and their concentration is decreasing with time, we will use a negative sign in their rate expression.

$$-\frac{1}{3}\frac{d[\mathrm{H_2}]}{dt} = -\frac{d[\mathrm{N_2}]}{dt}$$

On the other hand rate of formation of ammonia is twice the rate of consumption of nitrogen.

$$\frac{d[\mathrm{NH_3}]}{dt} = 2\frac{d[\mathrm{N_2}]}{dt}$$
$$\frac{1}{2}\frac{d[\mathrm{NH_3}]}{dt} = -\frac{d[\mathrm{N_2}]}{dt}$$

Corelaing both equation we can write

$$-\frac{d[\mathrm{N_2}]}{dt} = -\frac{1}{3}\frac{d[\mathrm{H_2}]}{dt} = \frac{1}{2}\frac{d[\mathrm{NH_3}]}{dt}$$

So, for a general chemical equation

$$\mathrm{aA + bB = cC + dD}$$

The rate expression with respect to each substrate will be like this

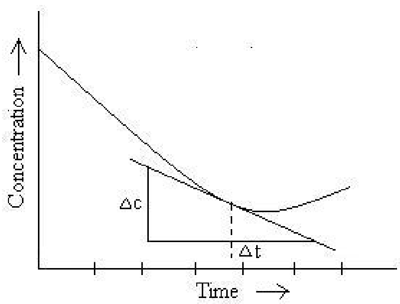
$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

2.6 Rate Law

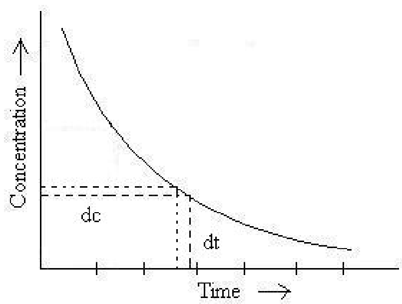
Rate law is the relation between rate of a reaction with concentration of reactants or products. The effect of stoichiometry of reactants and products are reflected in rate law of a chemical reaction. In a chemical reaction where more than one substrate are involved, the rate of the reaction will depend on each substrate but in the rate expression the power of the concentration of a particular substrate can't be written from stoichiometric equation of a reaction; it is purely an experimental fact. Rate of reaction can be calculate in different ways.

2.6.1 Calculation of instantaneous rate of a reaction

For instantaneous rate measurement of any reaction the small amount of reactants is taken at any instant after the reaction start and allowed to freeze it for analysis. Freezing is done for spontaneous stop of the reaction. A straight line graph is plotted with concentration of reactant or product against different time. Then, concentration of the compound at different time is plotted. The slope $\frac{\Delta C}{\Delta t}$ of the graph gives us the instantaneous rate of the reaction. There are so many instruments which can easily measure the instantaneous rate of any fast reaction.



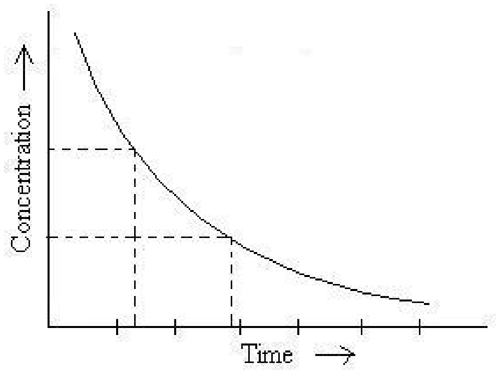
(a)Measurement of Instantaneous rate



(b)Measurement of Instantaneous rate

2.6.2 Calculation of average rate of a reaction

For average rate measurement of any reaction a small amount of reactant is taken at any instant after the reaction starts and allowed to freeze it for analysis. Again, a small amount of reactant is taken after some time of the first measurement in the same way. In this way we get different concentration data at different time . Then, concentration of the compound at different time is plotted. The ratio of change in concentration with the change in time at two different time gives us average rate of the reaction.



Measurement of average rate

Let in a chemical reaction, after 5 minutes the concentration of the reactant is 50 ML^{-1} and after 15 minutes the concentration of the reactant is 30 ML^{-1}. So, the change in concentration with the change in time-

$$\begin{aligned} \text{Average rate} &= \frac{30-50}{15-5}\ \text{M.L}^{-1}\text{minute}^{-1} \\ &= -\frac{20}{10}\ \text{M.L}^{-1}\text{minute}^{-1} \\ &= -2\ \text{M.L}^{-1}\text{minute}^{-1} \end{aligned}$$

2.6.3 Law of mass action :

The rate of any chemical reaction at any instance is directly proportional to active mass of the reacting species at that instance. Active mass is the activity of the reacting species and it is expressed in terms of moles/liter.

$$\begin{aligned} \text{For a chemical reaction, aA + bB + cC} &\rightarrow \text{products} \\ \text{The experimentally derived rate law can be written as,} & \\ \text{Rate}(-\frac{dc}{dt}) &\propto C_A^p C_B^q C_C^r \\ (-\frac{dc}{dt}) &= k.C_A^p C_B^q C_C^r \end{aligned}$$

Where C_A, C_B and C_C are the concentration of substrate A, B and C respectively at a time t and k is rate constant of the reaction. Now, if the concentration of all reactants are unity, i.e; 1 $mole.lit^{-1}$, then-

$$\text{Rate} = \text{k (rate constant).}$$

So, rate constant is the rate of a reaction where concentration of al reactants are unity. Though rate of any reaction depend upon many factor but rate constant depends only on **temperature.**

2.6.4 Order and molecularity of chemical reaction

$$\begin{aligned} \text{For a chemical reaction, aA + bB + cC} &\rightarrow \text{products} \\ \text{The experimentally derived rate law can be written as,} & \\ \text{Rate}(-\frac{dc}{dt}) &\propto C_A^p C_B^q C_C^r \\ (-\frac{dc}{dt}) &= k.C_A^p C_B^q C_C^r \end{aligned}$$

Where C_A, C_B and C_C are the concentration of substrate A, B and C respectively at a time t and k is rate constant of the reaction. p, q, and r are power or exponent on the concentration term in the rate equation and the sum of the power or exponent is called order of the reaction with respect to A, B and C respectively. The overall order of the reaction will be expressed as-

$$\text{order(n)} = p + q + r$$

So overall order of a reaction is the sum of all powers or exponent on the concentrations term used in a rate expression. Importantly order of a reaction has no relation with the stoichiometry of the reactants or products of a balanced chemical equation. Order is purely an experimental fact and it can be zero, any integer, fraction or negative value. Generally common chemical reactions are zero to third order maximum. Order of a chemical reaction gives some idea about the reaction mechanism. Molecularity of a reaction is the sum of the reacting particle take part in the reaction. Basically the sum of the stoichiometric number of the reactant molecules of a balanced chemical reaction is called molecularity. It is always a positive integer and never be zero or fraction. Molecularity do not give any idea about the mechanism of the reaction.

$$\text{For a chemical reaction like , aA + bB} = \text{cC + dD}$$

molecularity = (a + b)
For an elementary reaction order = molecularity but for a complex reaction they differ. For a multistep reaction, the order of the whole reaction will be the order of the slowest step as slowest step is the rate determining step.

$$\begin{aligned} 2HI &\rightarrow H_2 + I_2 \\ \text{Rate} &= k[HI]^2 \end{aligned}$$

For this reaction the order and the molecularity is same.

$$\begin{aligned} 2N_2O_5 &\rightarrow NO_2 + O_2 \\ \text{Rate} &= k[N_2O_5] \end{aligned}$$

For this reaction the order and the molecularity is not same.

2.6.5 Difference between order and molecularity

Order	Molecularity
1. It is sum of all powers or exponent on the concentrations term used in a rate expression. 2. It is purely experimental value. 3. Value determined from the rate equation. 4. it can be zero, any integer, fraction or negative value. 5. For a multi step reaction there is only one order throughout the whole reaction.	1. It is the sum of the reacting particle take part in the reaction. 2. It is purely theoretical value. 3. Value determined from the balance chemical equation. 4. It is always a positive integer and never be zero or fraction. 5. For a multi step reaction each elementary step has individual molecularity.