CHEMICAL KINETICS

Chemical kinetics deals with the rates of chemical reactions and with how the rates depends on factors such as concentrations and temperatures. Such studies are important in providing essential evidence as to the mechanism of Chemical process. Valuable evidence about ~~mechani~~ mechanisms also is provided by nonkinetic investigations — such as the detection of reaction intermediates and isotope exchange studies — but knowledge of a mechanism can be satisfactory only after a careful kinetic investigation has been carried out. ~~Kineti~~ Kinetic studies cover a very wide range, from several points of view.

Chemical reactions occur in the gas phase, in solution in a variety of solvents, at gas-solid and other interfaces, in the liquid state and in the solid state. Kinetically reactions ~~are~~ may be classified in two groups;

i) Homogeneous Reaction :— If the reaction takes place in one phase; is called homogeneous reaction. eg.

$$CH_3COOCH_3 + OH^- \longrightarrow CH_3COO^- + CH_3OH$$

ii) Heterogeneous Reaction :— If a reaction takes place in two or more phases, ~~or~~ is called heterogeneous reaction.

eg. $2HI \xrightarrow{Au(Cat)} H_2 + I_2$.

Many reactions are greatly influenced by the presence of foreign substance; ie; catalysts. Also ~~some~~ some reaction rates are accelerated by absorption of specific light waves; which are called photochemical reaction.

Most rate measurements are made on systems that are in thermal equilibrium, which means that energy is distributed among the molecules according to Boltzmann distribution. Experiments of this kind can be reffered to as 'bulk' or 'bulk' experiments. Theses branches of kinetics are described ~~as~~ as macroscopic kinetics, since the results relate to the behavior of a very large group of molecules in thermal equilibrium. During recent years kinetic studies provides some chemical reactions in which the reacting molecules are in well-defined states. Such studies are reffered to as microscopic. A very important technique in this field is that of crossed molecular beams. If a bimolecular ~~a~~ reaction $A + B \longrightarrow C + D$ is to be

studied, each reactants A & B is formed into a beam, characterized by well-defined velocities and internal energy states. The beams are made to cross one another so that some reactions take place. The directions of motion of the reaction products and of the unreacted A & B molecules are then determined, together with their velocities and internal energy states. Investigation of this kind provides valuable information about the dynamics of both reactive and unreactive collisions, because ~~of the~~ results of well-defined collisions are being observed.

Difference Between Chemical Kinetics And Thermodynamics :-

i) Classical thermodynamics does not provided any answer as time is not a variable in this case.

But chemical kinetics deals with the time factor.

ii) Thermodynamics is concerned only with the reactants and products of the reaction and does not pay any attention to intermediate of a reaction.

But chemical kinetics is concerned with detail of a chemical reaction, the mechanism of a reaction.

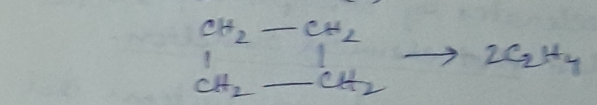
Classification of Chemical Reaction :-

Reactions mainly are of two types:

i) **Elementary Reaction**: Elementary reaction is a simple, step forward reaction. eg.

$$H_2 + I_2 \longrightarrow 2HI$$

$$Na(g) + Cl(g) \longrightarrow NaCl$$



$$\longrightarrow 2C_2H_4$$

Cyclo butane

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

ii) **Multistep ~~Rate~~ Reaction**:

Multistep reaction occur more than one step. The slowest ~~step~~ elementary step determine the rate of the reaction. So, this slowest step is known as rate determining step or R.D.S. eg.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Step I: $N_2O_5 \longrightarrow NO_2 + NO_3$ (fast)

Step II: $NO_3 + NO_2 \longrightarrow NO + O_2 + NO_2$ (Slowest) ⇒ R.D.S

Step III: $NO + NO_3 \longrightarrow 2NO_2$ (fast)

Extent of Reaction or Degree of Advancement :-

For any reactant or product in a reaction having time-independent stoichiometry the extent of reaction or degree of advancement is defined by

$$\boxed{\xi = \frac{n - n^\circ}{\nu}}$$

where $n^\circ \rightarrow$ initial amount of substance

$n \rightarrow$ amount of substance at time t

$\nu \rightarrow$ stoichiometric coefficient for that particular species in the particular equation that is written down for the reaction.

eg. $aA + bB + \cdots \longrightarrow \cdots + yY + zZ$

The extent of reaction $\xi = \frac{\Delta n_Y}{y} = \frac{\Delta n_Z}{z} = \frac{\Delta n_A}{-a} = \frac{\Delta n_B}{-b}$

Rate of Reaction :-

Rate of consumption and formation are not the same in general for all substances involved in a chemical reaction. It is convenient to define a rate that is the same for all species. For a reaction showing time-independent stoichiometry this can be done in terms of extent of reaction. Therefore, the rate of reaction is defined as Rate $(r) = \frac{1}{V}\frac{d\xi}{dt} = \frac{d\dot{\xi}}{V}$

For ith species $\dot{\xi} = \frac{1}{\nu_i V}\frac{dn_i}{dt}$ $\qquad aA + bB \longrightarrow yY + zZ$

Thus for general reaction $r = \frac{-1}{aV}\frac{dn_A}{dt} = -\frac{1}{bV}\frac{dn_B}{dt} = \frac{1}{yV}\frac{dn_Y}{dt} = \frac{1}{zV}\frac{dn_Z}{dt}$

The (-)ve sign indicate the decrease of amount of reactant A & B.

If the volume does not change during the course of the reaction then $\frac{dn_i}{V}$ may be replaced by dc_i where, c_i is the concentration of ith species.

$\therefore$ Rate $r = \frac{1}{\nu_i}\frac{dc_i}{dt}$

$\therefore r = -\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} = \frac{1}{y}\frac{dC_Y}{dt} = \frac{1}{z}\frac{dC_Z}{dt}$.

$\therefore$ Unit of rate is $\Rightarrow$ SI $\Rightarrow$ mol $m^{-3} s^{-1}$

& CGS $\Rightarrow$ mol $cm^{-3} s^{-1}$

Emperical Rate Equation :-

According to mass action law

rate $(r) \propto$ (active mass of reactant)$^\alpha$, active mass may be replaced by concentration.

$\therefore r \propto$ (concentration of reactant)$^\alpha$.

∴ For a reaction $aA + bB \rightarrow$ Product

$r \propto C_A^{\alpha} C_A^{\beta}$ where k is proportionality rate constant

$r = k C_A^{\alpha} C_B^{\beta}$

When $C_A = C_B = 1$, then $r = k$, here k is called specific rate constant; i.e. specific rate constant may be defined as rate at ~~constant~~ unit concentration of reactant.

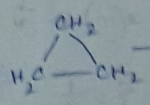
Order of Reaction :-

The exponance of the above equation α & β is known as order of ~~reaction~~ the corresponding components & $(\alpha+\beta)$ is the overall order of the reaction.

The order of reaction may be defined as the sum of the exponance of the concentration terms in the rate equation.

The order of reaction is purely an experimental quantity and it is not ~~nece~~ necessarily connected with the chemical equation of reactant reaction. In the case of elementary reaction the order is connected with the chemical equation. e.g. $H_2 + I_2 = 2HI$

The order of reaction may be zero, integer or fraction.

First order $\Rightarrow r = k C_A^{1}$ e.g.  $\rightarrow CH_3-CH=CH_2$

2nd " $\Rightarrow r = k C_A^2$

or

$r = k C_A C_B$ e.g. $H_2 + I_2 \rightleftharpoons 2HI$.

Fractional order $\Rightarrow$ ~~r = kE~~ $r = k C_{CH_3CHO}^{3/2}$ eg. $CH_3CHO \rightarrow CH_4 + CO$.

UNIT OF RATE CONSTANTS FOR DIFFERENT ORDER REACTION:

1st order : $k = \frac{r}{C_A} = \frac{mol\ lit^{-1} s^{-1}}{mol\ lit^{-1}} = s^{-1}$

2nd " : $k = \frac{r}{C_A^2} = \frac{mol\ lit^{-1} s^{-1}}{mol^2\ lit^{-2}} = mol^{-1} lit\ s^{-1}$

3rd " : $k = \frac{r}{C_A^3} = \frac{mol\ lit^{-1} s^{-1}}{mol^3\ lit^{-3}} = mol^{-2} lit^2 s^{-1}$

~~0th~~ zero-th " : $k = r = mol\ lit^{-1} s^{-1}$

Molecularity :-

At present there is no universal expected definition of molecularity. Two definitions are formed -

i) CLASSICAL DEFINITION :- Molecularity may be defined as the total number of molecules of the reactant

taking part in the simplest chemical reaction. It depends on the overall reaction.

eg. $A + 2B \rightarrow 3C$

$2A + 4B \rightarrow 6C$ ⇒ this is not the simplest ~~the~~ step of the reaction so, the molecularity of the reaction is $(1+2) = 3$.

<u>MODERN DEFINITION</u> :- Molecularity may be defined as the number of reactant molecules taking part in the slowest elementary step of a chemical reaction.

Molecularity is always an integer. It never be equal to zero or fraction. For an elementary reaction order and molecularity is equal.

<u>First-Order Reaction</u> :-

A reaction that is first order with respect to a reactant A and is zero order with respect to any other reactants may correspond to various stoichiometry, such as, $A \rightarrow P$, $A \rightarrow 2P$, $2A \rightarrow P$, $A + B \rightarrow P$, $2A + B \rightarrow P$.

~~Say~~, Suppose a reaction $A \rightarrow P$

$t = 0$	a	0
$t = t$	$(a-x)$	x

Say, at initial time; i.e; $t = 0$, the concentration of A is a or $[A]_0$ or C_0 & then conc. of P is 0. After a certain time t the concentration of A decreases to $(a-x)$ or C_A & that of P increases to x or C_P.

∴ The rate of the reaction is —

$$-\frac{dC_A}{dt} = k C_A \quad [k \rightarrow \text{first order rate constant}]$$

$$\text{or } -\frac{d(a-x)}{dt} = k(a-x)$$

as a is constant $\frac{dx}{dt} = k(a-x)$

$$\text{or } \int \frac{dx}{a-x} = k\int dt$$

$$\text{or } -\ln(a-x) = kt + c \quad [c \rightarrow \text{integration constant}]$$

At time $t = 0$, $x = 0$

$$\therefore -\ln a = c.$$

$$\therefore -\ln(a-x) = kt - \ln a$$

$$\text{or } \ln a - \ln(a-x) = kt$$

$$\text{or } kt = \frac{\ln a}{\ln(a-x)} \quad \text{or } \boxed{k = \frac{1}{t}\ln\frac{a}{(a-x)}}$$

$$\text{or } t = \frac{1}{}$$

or, L