CHEMICAL KINETICS:

Chemical kinetics constitutes an important topic in physical chemistry. It concern itself with measurement of rates of reactions proceeding under given conditions of temperature, pressure and concentration.

Thermodynamics predicts that at room temperature hydrogen and oxygen react to form water, all the reactants being essentially converted into the product. But when we actually carry out the experiment we find that the reaction takes place so slowly that unless we are willing to wait indefinitely, practically ho water results. On the other hand, experiment shows that N_2O_4 decomposes into NO_2 under atmospheric conditions almost instantaneously even though -AG°, which is a measure of the spontaneity of a reaction, is far less for the decomposition of N_2O_4 than that for the reaction between hydrogen and oxygen to form water. These two examples suggest that there is essentially no correlation between thermodynamic instability and the rate of a chemical reaction. Infact, the rate of a reaction depends upon structural and energetic factors which are not uniquely specified by thermodynamic quantities such as the free energy change. Hence, chemical kinetics is a technique complimentary to thermodynamics for studying a given reaction.

The first stage in studying the rate and mechanism of a chemical reaction is the determination of the overall stoichiometry of the reaction and to identify any side-reaction. The next step involves the determination of the change of the concentrations of the reactant and product species with time. Since the reaction rate depends sharply on temperature, the temperature of the reacting mixture must be kept constant.

Several experimental techniques have been developed to monitor the concentrations of the reactants and the products and their variation with time. The selection of a typical method depends on the nature of the species involved and how rapidly their concentrations change. For reactions that are relatively slow, conductometric, potentiometric, optical methods, polarimetry and spectrophotometry are usd. For reactions in which one or more of the products are gases, the, reaction rate involves monitoring pressure.

Reactions in solution involving ionic species may be studied by monitoring their conductivity. Spectrophotometry involving measurement of the intensity of absorption in a particular spectral region, is widely used to monitor concentration. This technique is particularly useful when one substance in the reaction mixture has a strong characteristic absorption in a conveniently assessible region of the spectrum. Reactions that involve a change in the concentration of. H+ ions may be studied by monitoring the pH of the solution with a glass electrode. Other methods of monitoring the composition include mass spectrometry, gas chromatograpy and magnetic resonance {both NMR (Nuclear magnetic resonance) and EFR (electron paramagnetic resonance, also called ESR i.e. electron spin resonance).

In a real-time analysis, the composition of the reaction mixture is analyzed while the reaction is in progress by a suitable method. In the quenching method, the reaction is stopped after

being allowed to proceed for a certain time and the composition is analyzed. The entire reaction, mixture may be quenched either by sudden coolling or by adding it to a large volume of the solvent. This method is applicable for reactions that are slow enough so that there is little reaction during the time it takes to quench the reaction mixture.

The Rate Equation:

Consider a simple hypothelical reaction of the type

A $\longrightarrow$ P
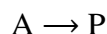
The rate of the reaction at any given time will depend upon the concentration of the reactant A at that time. As the reaction progresses, the concentration of A keeps on falling with time. The rate of the reaction at any given instant is given by the expression

$r = \frac{-dc_A}{dt} = k_{CA}$ ... (1)

where $-dc_A$ is the infinitesimally small decrease in the concentration of A in an infinitesimally small interval of time dt, c_A gives the concentration of the reactant A at the given constant and k is a constant called the rate constant or velocity constant of the reaction.

The concentration of the product p goes on increasing with time. Hence the rate of the reaction can also be expressed in terms of increase in concentration of the product P as well. Thus,
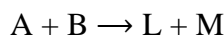
$r = \frac{dc_p}{dt} = k_{cA}$ ... (2)

where dc_p is an infinitesimilarly small increase in the concentration of the product P in the concentration of the product P in an infinitesimally small interval of time dt.

From Eqs. 1 and 2

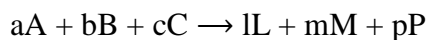$r = \frac{-dc_A}{dt} = \frac{dc_p}{dt} = kc_A$ ... (3)

For a reaction of the type

A + B $\longrightarrow$ L + M

the reaction rate can be expressed as

$r = \frac{-dC_A}{dt} = \frac{-dC_B}{dt} = \frac{dC_L}{dt}$

$= dc_M/dt = k_{cA\ cB}$ ... (4)

consider a general reaction of the type,

aA + bB + cC $\longrightarrow$ lL + mM + pP

The rate of this reaction, according to the law of mass action, is given by r = rc$_A{}^a$ c$_B{}^b$ c$_C{}^c$

The rate of such a reaction is to be expressed in terms of fallen concentration of a reactant per mole or increase in concentration of-a product per mole. Accordingly,

$r = \frac{-1}{a}\frac{dc_A}{dt} = -\frac{1}{b}\frac{dc_B}{dt} = -\frac{1}{c}\frac{dc_C}{dt}$

$= \frac{1}{l}\frac{dc_L}{dt} = \frac{1}{m}\frac{dc_M}{dt} = \frac{1}{p}\frac{dc_p}{dt} = kC_A^a C_B^b C_C^c$ ... (5)

Rate constant or velocity constant:

For a general reaction of the type:

aA + bB + cC $\longrightarrow$ products,

$r = kc_A{}^a\ c_B{}^b\ C_C{}^c$ ... (6)

If $c_A = c_B = c_C = 1$, then r = k. Thus at a given temperature, the rate constant or velocity constant of a reaction, fn general is equal to the rate of the reaction when the concentration of each of the reactants is unity.

Order of a Reaction:

In the study of chemical kinetics, reactions are generally classified terms of their order. The order of a reaction is defined as the number of molecules whose concentrations determine the

rate of the chemical reaction at a given temperature.

Alternatively, we may define the order of a reaction as the sum of the powers to which the concentration (or pressure) turns are raised in order to determine the rate of the reaction. Thus a reaction is said to be of the first order if its rate is given by the expression of the type.

$r = k_1 c_A$;

of the-second order it the rate is given by the expression of the type:

$r = k_2 c_A^2$ or

$r = k_2 \, c_A \, c_B$

of the third order it the fate is given by the expression; of the type.

$r = k_3 C_A^3$ or $r = k_3 c_A^2 c_B$ or

$r = k_3 C_A C_B^2$ or $r = k_3 c_A^2 c_B c_C$ and

so on.

For a zero order reaction, the rate equation is written as $r = k_0$.

• The order of a reaction may not always be a whole number. It can be a fractional quantity also. It is particularly so in heterogeneous reactions.

Integration of Rate expression for First-order Reactions:

The differential, rate expression for the first order reaction,

$A \longrightarrow p$ is diven by

$r = -d[A]/dt = d[p]/dt = k[A]$

 ... (7)

Separating the variables, we get

$-d[A] / [A] = k, dt$

Replacing [A] by C_A for the sake of notational convenience, we have

$-d \, cA/cA = k, dt$

Before performing the actual integration, let us first ascertain the limits of integration.

Let the initial concentration at time t=0 be c_0.

Subsequently, at any other time, t_1 the concentration will be c.

On integration, we obtain

$\int_{c_0}^{c} -dc_A/c_A = k_1 \int_0^t dt$;

$[- \ln c]_{c_0}^{c} = k_1 [t]_0^t$

-ln $[c/c_0]= k_1 t$ or $c = c_0 e^{-k_1 t}$ ... (10)

From equation (10) we can write

$k_1 = \frac{1}{t} ln \frac{c_0}{C}$

Equation (11) gives the expression for the first-order rate constant, k_1.

Eq. 11 is usually written in another form. If initial concentration of the reactant is a and x moles of it react in time t_1 then-the concentration of the reactant left behind at time t will be a-x.

In such a case, $c_0 \propto$ a and $c \propto$ (a-x). Hence Eq. 11 takes the form
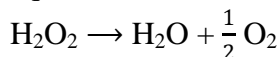
$k_1 = \frac{1}{t} ln \frac{c_0}{a-x}$

… (12)

For a first order reaction, the concentration of the reactant decreases and that of the product increases exponentially with time.

Examples of first order reaction:

1. Decomposition of hydrogen peroxide in aqueous solution

$H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$

The decomposition is catalysed by the addition of platinum. The progress of the reaction is followed by measuring the volume of oxygen evolved after different intervals of time. This can also be done by withdrawing a small amount of the solution and determining the unchanged concentration of the peroxide by

titrating against potassium permanganate, after different intervals of time. If the same volume of the solution is withdrawn after various intervals of time and the same solution of potassium permanganate is used as the tit-rant, the concentration of hydrogen peroxide, (a-x), at any instant, is given directly by the volume of the permanganate solution used. The volume of $KMnO_4$ used before the commencement of the reaction i.e. at zero time, gives the initial concentration (a) of hydrogen

2. Decomposition of ammonium nitrite in aqueous solution:

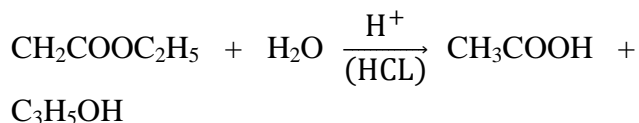$NH_4\ NO_2 \longrightarrow 2H_2O + N_2$
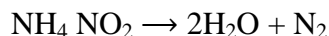
$K_1 = \dfrac{1}{t} \ln \dfrac{V_\infty}{V_\infty - V_t}$

V_t = Volume of nitrogen collected after the time t V_∞ = total volume collected at the end of reaction
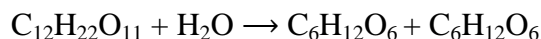
3. Hydrolysis of ethyl acetate:

Pseudo mono-molecular reaction:

$CH_2COOC_2H_5 \ + \ H_2O \ \xrightarrow[(HCL)]{H^+} \ CH_3COOH \ +$ C_3H_5OH

$K_1 = \dfrac{1}{t} ln \dfrac{V_\infty - V_0}{V_\infty - V_t}$

4. Inverstion of sucrose:

$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose $\qquad$ Glucose Fructoses

Dextro rotatory $\quad$ pextro $\quad$ Laevo

$K = \dfrac{1}{t} ln \dfrac{r_0 - r_\infty}{r_1 - r_\infty}$

r_0, r_1 and r_∞ represent rotations at the commencement of the reaction, after time t and at the end of the reaction, respectively.

Integration of Rate expressions for second-order Reactions:

Case I:

When both the reactants are the same.

$K_2 = \dfrac{1}{t} \left[\dfrac{1}{a-x} - \dfrac{1}{a} \right] = \dfrac{1}{t} \left[\dfrac{x}{a(a-x)} \right]$
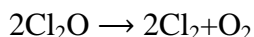
Case II:

When the reactants are different.

$K_2 = \left[\dfrac{1}{(b-a)t} ln \dfrac{a(b-x)}{b(a-x)} \right]$
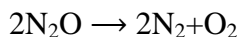
Examples of second order Reactions:

a) Gaseous Reactions:

1. Conversion of 6zon4 into, oxygen 100°C $20_3 \longrightarrow 30_2$

2. Thermal decomposition of chlorine monoxide at 200°C

$2Cl_2O \longrightarrow 2Cl_2 + O_2$

3. Thermal decompostion of nitrous oxide.

$2N_2O \longrightarrow 2N_2 + O_2$

b) Reactions, in solutions:

1. Saponification of esters:

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

2. Benzoin condensation:

$C_6H_5CHO + OHCC_6H_5 \qquad\qquad \longrightarrow$ $C_6H_5CH(OH)COC_6H_5$
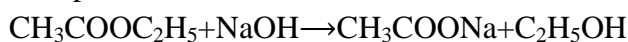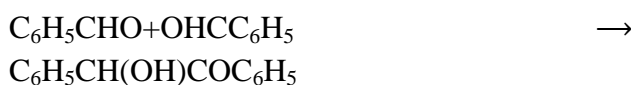
Benzaidehyde Belzaldehyde Benzoin

3. Conversion of ammonium cyanate into urea:

i) First stage:

$NH_4CNO\ NH_4NCO\ H\text{-}N\text{=}C\text{=}O + NH_3$

ii) Second stage:

4
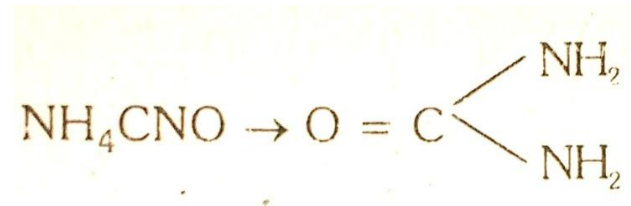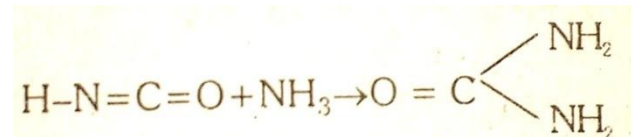
The second stage which is slow, determines the rate of the reaction.

Since it involves two molecules, the reaction, as a whole, behaves as second - order.

3. **(Integration of Rate expression for Third-Order Reactions)**

Let us consider a simple third - order reaction of the type

$3A \longrightarrow P$

$$K_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$$

4. Integration of Rate expression for zero-order reactions:

Examples are known of reactions in which the reaction rate Ts not affected by changes in concentrations of one or more reactants. These are called zero-order reactions. In such reactions, the rate may be determined by some other limiting factor such as the amount of catalyst used in a catalytic reaction or the intensity of light absorbed in a photochemical reaction.

Mathematically, for a zero-order reaction

$A \longrightarrow P$
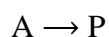
$r = -d\,[A]/dt = k_0$

where k_0 is the rate constant.

Rearranging,

$-d[A] = k_0\,dt$

If at $t = 0$, the initial concentration is $[A]_0$ and the concentration at $t = t$, is $[A]_1$ then, integration yields

$-\int_{[A]_0}^{[A]} d[A] = K_0 \int_{t=0}^{t=t} dt$ so that

$K_0\,t = [A]_0 - [A]$

$K_0 = ([A]_0 - [A])\frac{1}{t}$

The above equation is the integrated rate equation for a zero-order reaction.

Half-Life time of a Reaction:

In order to characterize the rate at which a chemical reaction may proceed, it is customary to introduce a convenient parameter called the half-time of the reaction. It is defined as the time required for the reaction to be half completed and is denoted by the symbol, $t_{1/2}$. It can be related to the corresponding rate constant.

1. $t_{1/2}$ for a first-order Reaction:

$t_{1/2} = 0.693/k_1$

2. $t_{1/2}$ for a second-order Reaction:

$t_{1/2} = \frac{1}{k_2 a}$

3. $t_{1/2}$ for a third-order Reaction:

$t_{1/2} = \frac{1}{2k_3 a^2}$

Methods for determining the ordr of a Reaction:

1. The use of Differential Rate Expressions
2. The use of Integral Rate Expressions.
3. The Half-life method
4. Isolation method

Molecularity of a Reaction:

The molecularity of a reaction should not be confused with its order.

Molecularity of a reaction is defined as the number of molecules involved in the step leading to the chemical reaction. If only one molecule is involved, the reaction is said to be unimolecular.
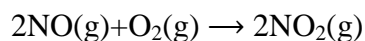
The example is the dissociation of nitrogen pentoxide.

$N_2O5(g) \longrightarrow N_2O_4(S) + \frac{1}{2}O_2(g)$
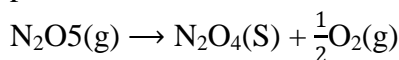
If two molecules are involved, the reaction is said to be bimolecular.

$2HI(g) \longrightarrow H_2(g) + I_2(g)$
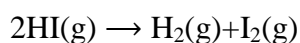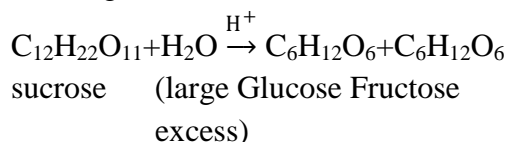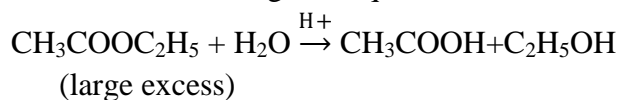
Similarly, if three molecules are involved the reaction is said to be trimolecular. Example is the oxidation of nitric oxide.

$2NO(g)+O_2(g) \longrightarrow 2NO_2(g)$

Order and Molecularity of Simple Reactions:

From a study of the kinetics of a number of simple reactions. We know that their order is the same as their molecularity. Thus the order of the reaction involving the decomposition of nitrogen pentoxide is 1. that of the reaction involving the dissociation of hydrogen iodide is 2 and that of the reaction involving combination of nitric oxide and oxygen is 3.

But this is not always the case. In several reactions, the order is different from molecularity. This is particularly so when one of the reactants is present in large excess. Examples: Hydrolysis of ethyl acetate and inversion of cane sugar in aqueous solutions.

$CH_3COOC_2H_5 + H_2O \xrightarrow{H+} CH_3COOH+C_2H_5OH$
      (large excess)

$C_{12}H_{22}O_{11}+H_2O \xrightarrow{H^+} C_6H_{12}O_6+C_6H_{12}O_6$
sucrose   (large Glucose Fructose
                excess)

The molecularity of each reaction is 2. The order of each reaction, however, is 1 since we know from experiment that the rate of the reaction varies directly as the concentration of ethyl acetate in the first case and that of sucrose in the second case.

The reason is that water is present in such a large excess that its concentration remains almost constant in the course of the reaction in each case. The rate of the reaction, therefore, varies only with the concentration of the ester in the first kye and that of sucrose in the second

case. Such reactions are known as pseudo-monomolecular reactions.

Order and Molecularity of complex Reactions:

Many reactions are known to occur in two or more steps. Such reactions from the point of view of chemical kinetics, are often termed as complex reactions. Each step of the reaction, however is a simple, reaction, i.e. an elementary reaction. Each elementary reaction has its own molecularity depending upon the number of molecules of the reactant or reactants taking part in that, reaction.

The order of a complex reaction is given by the order of the slowest step in the sequence of various steps involved in that reaction.

Effect of Temperature on Reaction Rates:

The ratio of the rate constants of a reaction at two temperatures differing by 10°C is known as the temperature coefficient of the reaction. The temperatures 3 usually selected for this purpose are 25°C and 35°C. Thus,

Temperature coefficient $= \frac{\text{Rate constant at } 35°C}{\text{Rate constant at } 25°C} = \frac{k_{35}}{k_{25}}$ The value of the temperature coefficient for most of the reactions is close to 2 and in some cases it approaches

Collision Theory:

According to this theory, for chemical reactions to occur, there must be collisions between the reactant molecules. However, most of the collisions taking place between the molecules are ineffective,. The important postulate of the collision theory is-that only those collisions result in chemical reaction in which the colliding molecules are associated with a certain minimum energy called, the threshold energy.

Activation energy:

The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy. Thus,

Activation Energy = Threshold energy-Energy actually possessed by molecules

Effect of catalyst:

A catalyst is a substance that can increase the rate of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction.

A catalyst does not alter the position of equilibrium in a reversible reaction. It simply hastens the approach of the equilibrium by speeding up both the forward and backward reactions.

The Arrhenius Equation:

Arrehenius proposed the following empirical equation for calculating the energy of activation of a reaction having rate constant k at temperature T.

$k = Ae^{EaRT}$ ...(14)

where E_a is called the Arrhenius activation energy and A is called the Arrhenius pre-exponential factor.

Since the exponential factor in eq. (14) is dimensionless, the pre-exponential factor A has the same units as the rate constant k. The units of k for a first - order reaction are s^{-1}, which is the unit of frequency. Hence A is also called the frequency factor. Ea and A are called the Arrhenius parameters.

$ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2-T_1}{T_1 T_2}\right]$ is called the integrated Arrhenius equation. Knowing the rate constants at two different temperatures, the energy of activation Ea can be readily determined.

Theories of Reaction Rates:

1. The collision theory of Bimolecuiar Gaseous reactions.
2. Activated Complex Theory (ACT) of Bimolecuiar Reactions.
3. The Lindemann Theory of Unimolecular Reactions.

Complications in the Determination of order of Reactions:

The study of chemical kinetics becomes highly complicated due to the occurrence of
i) Consecutive reactions
ii) Chain reactions
iii) Parallel or side reactions
iv) Reversible reactions

1. The rate constant for a first order reaction is $1.54 \times 10^{-3} s^{-1}$. Calculate its half-life time.
   Solutions:
   $t_{1/2} = 0.693 / k_1$
   $t_{1/2} = \frac{0.693}{1.54\times10^{-3} s^{-1}} = 450s$

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