① T.D.C 2nd Sem (Regular)

CHEMICAL KINETICS

Differential rate law and rate constant.

The mathematical expression describing the relation between the rate of the reaction and the concentration of the reactants is known as differential rate law.

According to the law of mass action, the rate of reaction is proportional to the ~~power~~ Product of a certain power of the molar concentration of the reacting species.

Let any general reaction be

$$aA + bB \rightarrow cC + dD$$

$$\text{rate} \propto [A]^{\alpha}[B]^{\beta} \rightarrow ①$$

Where α, β are the number of reacting species of A and B, $\alpha \leq a$ and $\beta \leq b$. In almost all the cases α and β are less than a & b respectively, because in any reaction all the reactants molecules do not take part in the reaction to give us the Product.

From ①

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = K[A]^{\alpha}[B]^{\beta} \rightarrow ②$$

The value of α and β may be whole numbers, fractions, zero or even negative in rare cases. The value of α and β can be determined only experimentally and cannot be derived by theoretical calculations.

In eqn ② K is a constant and called the rate constant. ~~The unit of K char~~

eqn ② is the differential rate equation for the general reaction, which may be written completely as

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

Order and Molecularity of a reaction :-

Order of a reaction :- It is defined as the sum of the exponents (powers) to which the molar concentration terms in the rate law are raised to express the observed rate of a reaction.

For Example for a reaction

$$aA + bB \rightarrow \text{Product}.$$

The rate eqn is $\text{rate} = K[A]^{\alpha}[B]^{\beta}$.

where α and β are the reacting species of A and B

then the order of the reaction is $(\alpha + \beta)$.

The order of a reaction may be a whole number, fraction or zero. The order for a reaction can only be determined experimentally.

Some examples.

(1) $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$ [1st order reaction].

$\text{rate} = -\frac{d[N_2O_5]}{dt} = K[N_2O_5]^1$

(2) $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$ [2nd order reaction]

$\text{rate} = K[CH_3COOC_2H_5]^1[NaOH]^1$

$\text{order} = 1+1 = 2$

(3) $2NO + O_2 \rightarrow 2NO_2$ [3rd order reaction]

$\text{rate} = K[NO]^2[O_2]^1$

$\text{order} = 2+1 = 3$

(4) Reaction of zero oder. - In these reactions, the concentration of the reactants do not influence the rate of the reactions, because they do not change during the reaction. e.g the combination of H_2 and Cl_2 to form HCl, over the surface of water at constant pressure.

(5) Reaction of fractional order

$$CH_3CHO \rightarrow CH_4 + CO$$

$\text{Rate} = K[CH_3CHO]^{3/2}$ The order is $3/2$

Molecularity of a reaction :- It may be defined as the number of reacting species (molecules, atoms or ions) which collide simultaneously to bring about a chemical reaction.

Characteristics of molecularity :-

1. Molecularity pertains to a single step reaction or a single step of a complex reactions which involves a number of steps for its completion. Molecularity of such reactions as a whole has no meaning.
2. Molecularity is always a whole number and is never in fraction or zero.
3. The molecularity of a single step reaction or a step of a reaction does not exceed three.

Pseudo Unimolecular reactions :- Let us consider the reaction

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

In this reaction usually the order of the reaction should be 2. But in the reaction a large excess of water is taken as a reactant, so that the concentration of water remains virtually constant and the reaction follows first order kinetics. This type of reactions are termed as pseudo first order reaction or pseudo unimolecular reaction.

Integrated Rate law :- ~~Zero order~~ To get a relationship between rate constant, concentration and time, we need to integrate the rate equation. The relation obtained is called integrated rate equation or integrated rate law.

Integrated rate equation for zero order reaction

In this type of reaction the rate of the reaction does not depend upon the concentration of the reactant.

$$A \rightarrow P$$

$$\text{Rate} = -\frac{d[A]}{dt} = K_0[A]^0 = K_0 \rightarrow (1)$$

Let $[A]_0$ be the concentration of A at $t=0$ and $[A]$ is the concentration at time t. ~~Integr~~

or $-d[A] = K_0 dt$

integrating $\int -d[A] = K_0 \int dt$

$= ~~[A]_0~~ \quad [A] = -K_0 t + I$ (I is the integration constant) $\rightarrow (2)$

At $t=0$, $[A] = [A_0]$.

Putting this value in equation (2)

$I = [A_0]$

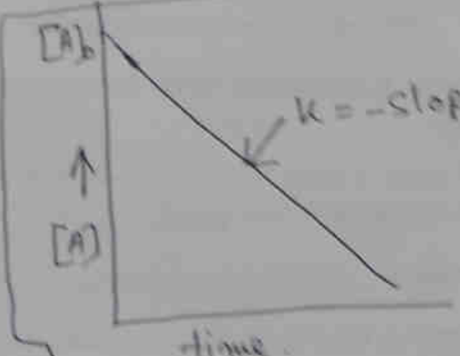
$[A] = -K_0 t + [A]_0$

$$\boxed{K_0 = \frac{[A]_0 - [A]}{t}} \rightarrow (3)$$

Characteristics of zero order reaction :-

(I) Unit of K_0 is $mol\ L^{-1} s^{-1}$.

(II) A plot of $[A]$ vs t will be a straight line with a negative slope



Concentration vs time plot for zero order reaction.

(III) Half life Period $(t_{1/2})$ of zero order reaction.

At $t_{1/2}$, $[A] = \frac{1}{2}[A]_0$

From eqn (3)

we get $t_{1/2} = \frac{1}{K_0}\left[[A_0] - \frac{[A_0]}{2}\right]$

$$t_{1/2} = \frac{1}{2K_0} \rightarrow (4)$$

Half life Period of a reaction :— Half life period is the time during which the concentration of the reactant falls down to half of its initial value,

Integrated rate law of 1st order reaction.

For a 1st order reaction

$$A \longrightarrow Product.$$

The rate is

$$rate\,(v) = K\,[A]^{1} \rightarrow (1)$$

$$-\frac{d[A]}{dt} = KA.$$

Or
$$\frac{d[A]}{[A]} = -K\,dt \rightarrow (2)$$

Let $[A]_0$ be the initial concentration of $[A]$ at $t=0$

and $[A]$ is the concentration at time t, Then.

$$\int \frac{d[A]}{[A]} = -k\int dt$$

$$\Rightarrow \ln[A] = -kt + I \rightarrow (3)$$ where I is the integration

constant. when $t=0$; $[A]=[A]_0$

Or $+\ln[A_0] = I$

Putting the value of I in equ^n (3)

$$\Rightarrow \ln[A] = -kt + \ln[A_0]$$

$$\Rightarrow \ln[A]_0 - \ln[A] = kt.$$

$$\Rightarrow \ln\frac{[A]_0}{[A]} = kt$$

$$\boxed{K = \frac{1}{t}\ln\frac{[A]_0}{[A]} = \frac{2.303}{t}\log\frac{[A]_0}{[A]}.}$$

It is the rate expression for a 1st order reaction,