**1.5 Zero Order Kinetics** A chemical reaction whose rate does not depend on concentration of reactants is called a zero order chemical reaction.

The rate of the reaction can be written as dx/ dt = Constant

⇒ dx dt = K

or, dx = K dt

On integration, = K

 or, x = Kt + C (Integration Constant).

When t = 0, x = 0 hence C = 0

 So, x = Kt

Or, K = x t

A plot of x versus t should give a straight line passing through the origin as shown in the figure and the slope of this straight line is K.



Example: Photochemical combination of H2and Cl2to form HCl. The rate of this reaction does not depend on concentration

**1.6 First Order Kinetics:** A reaction of the first order is represented as

 X → Y

where X is the reactant and Y the product. The rate of the reaction will be directly proportional to the concentration i.e.,

 − = K C

in which C is the concentration of the reactant at any time t and K is a constant, called the velocity constant or specific reaction rate.

Thus− = K dt

On integration − = K

 −ln c = kt +C(Integration Constant).

If at the start of the reaction the initial concentration of the reactant is Co then we have at t = 0 , C = Co Substituting −ln Co = C

 −lnC = Kt −ln Co

 ln = Kt

Or = e −Kt

Or C = Coe –Kt

 The concentration C therefore diminishes exponentially with time. We may also write

 Co −C = Co(1−e −Kt)

 The rate equation may also be conveniently expressed in an alternative form, by expressing the rate in terms of the product. When x moles per unit volume of product Y is formed from the reactant, the concentration of the reactant is (a − x), where a is the initial concentration of the reactants. So

Or

 On integration

or, (Integration Constant) When t = 0, x = 0,hence

The fractional extent of the reaction at any time t is

When the initial concentration ais not known but the concentrations at two intervals t1 and t2 are known, the rate equation can be derived. If x1 and x2 are the concentrations of product at t1 and t2, the corresponding concentrations of reactants would be (a- x1) and (a-x2).

So and

***Characteristics***

1) In a first order reaction C =Coe −Kt, the reaction cannot be complete because C would become zero at infinite time.

2) The quantity is a ratio of concentrations, so, its value will be the same what ever units are employed to express the concentrations e.g. moles/litre, gms/c.c etc. It shows that the velocity constant will have the dimension of reciprocal time, Sec−1

3) The equation is

If is plotted graphically against time, it would give a straight line. So when a plot constructed from experimental values of and t is found to be linear, the reaction is of the first order. The slope of the line is – from which the velocity constant K can be determined.



4) The time required for half the reactant to change can be easily evaluated. Let t1 /2 be the time required when x = a/2 . Then

=

The period of half decomposition is thus constant for a given reaction and is independent of initial concentration. The time required is called half value period or half life in case of radioactive changes. The time necessary to complete any definite fraction (ϕ) of the reaction is independent of the initial concentration in first order kinetics, for tφ = .