CLASS 12
CHAPTER 4

CHEMICAL KINETICS

Chemical Kinetics

The branch of chemistry, which deals with the study of reaction rates and their mechanisms, called *chemical kinetics.*

Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction.

Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered.

The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction.

Rate of a Chemical Reaction

The speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. It can be expressed in terms of:

(i) the rate of decrease in concentration of any one of the reactants, or
(ii) the rate of increase in concentration of any one of the products.

The rate of the reaction = <u>Change in concentration of R or P</u>
                                                Time taken
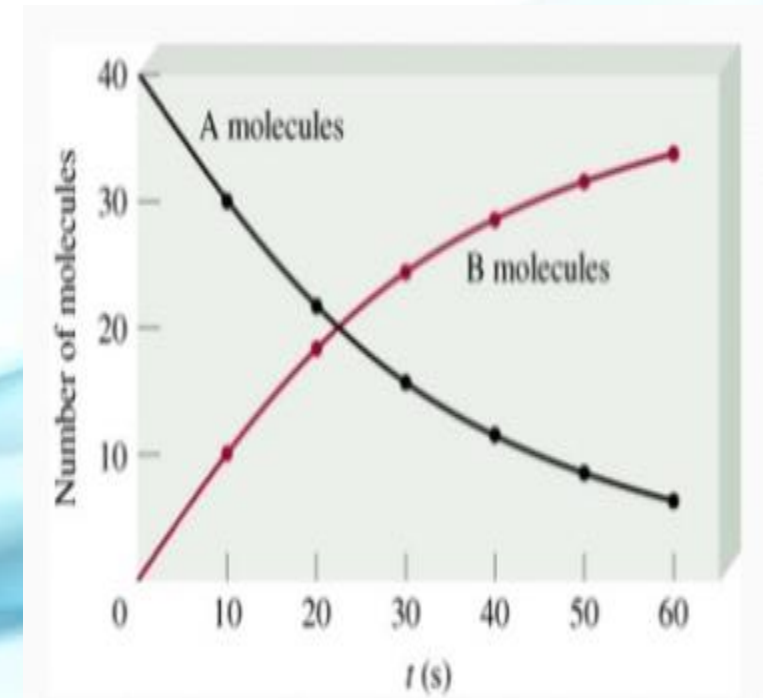
Average rate & Instantaneous rate

❑ **Average rate of reaction is the rate measured for larger change in concentration (or) the rate measured for longer time intervals.**
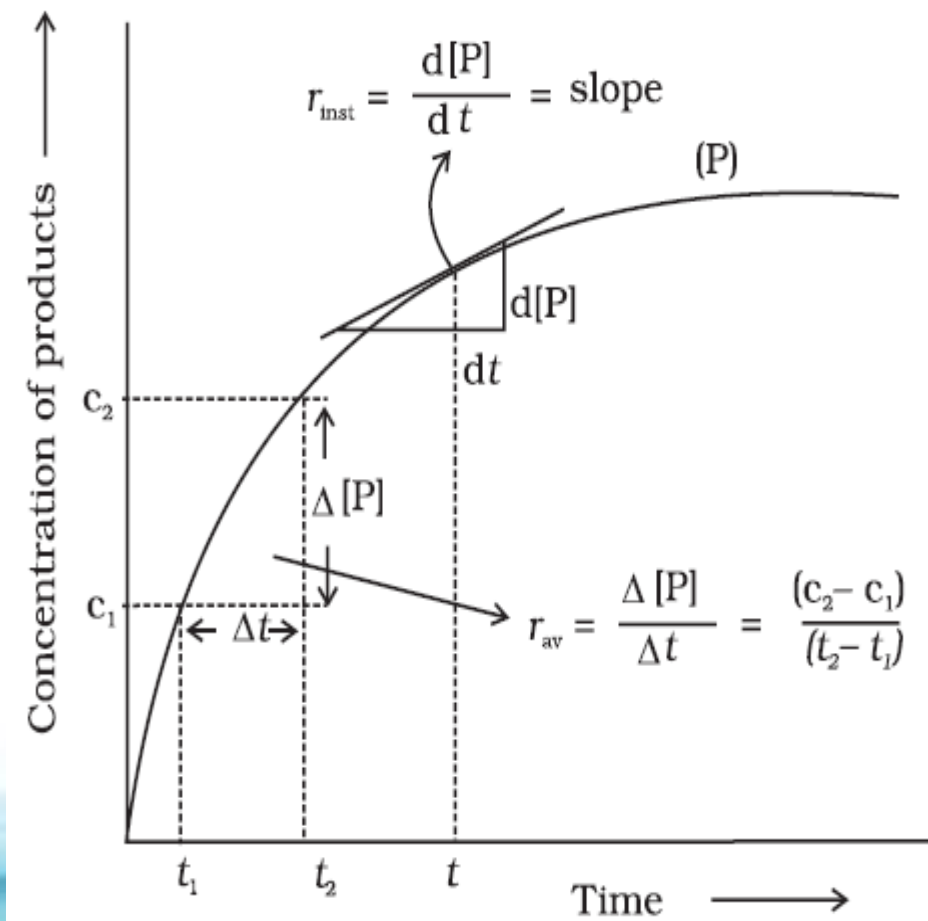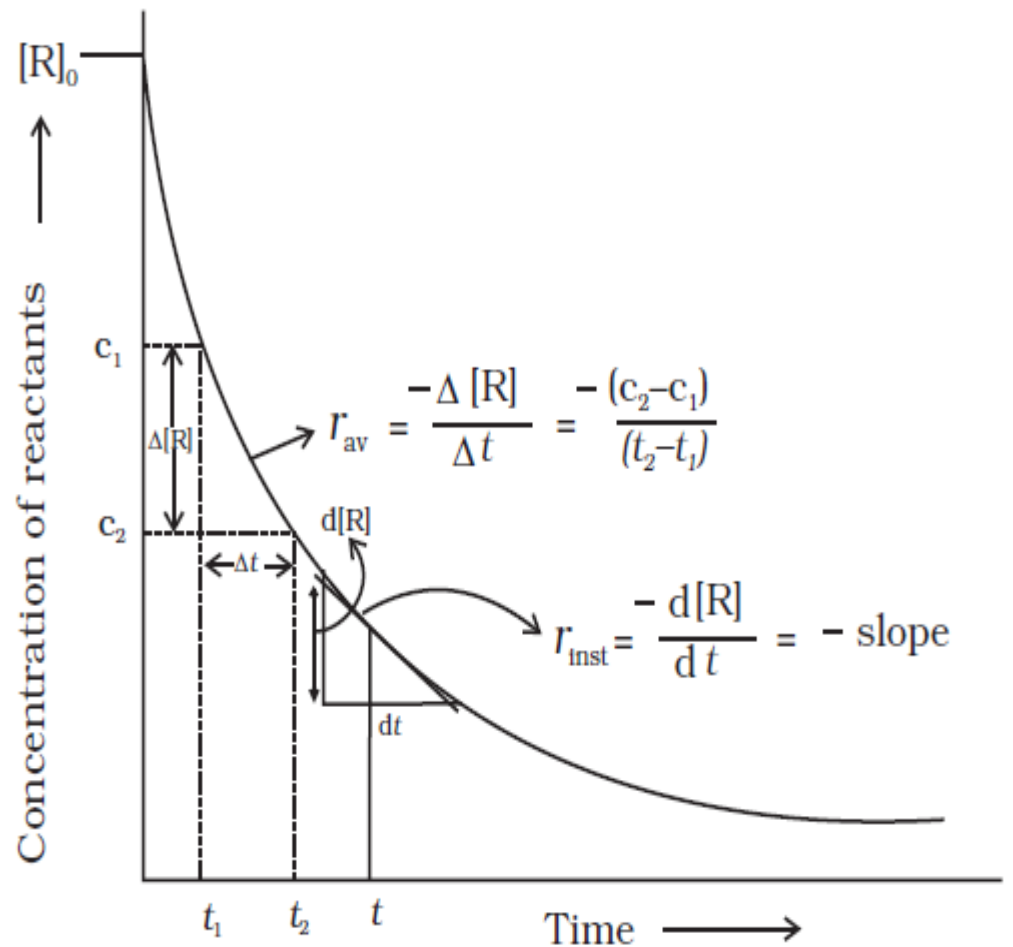
$$\text{Average rate of reaction} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

❑ **The rate of reaction at a particular instant of time is called as the instantaneous rate,**

$$\text{Instantaneous rate of reaction} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

❑ *It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero).*

Average rate & Instantaneous rate

The Rate Expression of a Chemical Reaction

Consider a general reaction,

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of reactant and product respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

$\Delta t = t_2 - t_1$ $\Delta[R] = [R]_2 - [R]_1$ & $\Delta[P] = [P]_2 - [P]_1$

The average rate of the reaction $= \dfrac{- \Delta[R]}{\Delta t} = \dfrac{\Delta[P]}{\Delta t}$

The instantaneous rate of the reaction $= \dfrac{- d[R]}{dt} = \dfrac{d[P]}{dt}$

The Rate expression of a Chemical Reaction

- **Rate of disappearance of Reactant = Rate of reaction**

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta [R]}{\Delta t}$$

Rate of appearance of Product = Rate of reaction

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{\Delta [P]}{\Delta t}$$

Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity.

- **Consider the reaction**

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Rate of reaction = $-\dfrac{\Delta[N_2]}{\Delta t} = -\dfrac{\Delta[H_2]}{3 \times \Delta t} = \dfrac{\Delta[NH_3]}{2 \times \Delta t}$
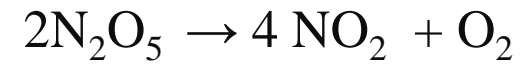
Rate of disappearance of N_2 = Rate of reaction

Rate of disappearance of H_2 = 3 x Rate of reaction

Rate of appearance of NH_3 = 2 x Rate of reaction

Q. Write the average and instantaneous rate expressions for the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2.$$

$$2N_2O_5 \rightarrow 4\,NO_2 + O_2$$

Average rate of reaction $= -\dfrac{\Delta\,[N_2O_5]}{2\times\Delta t} = -\dfrac{\Delta\,[NO_2]}{4\times\Delta t} = \dfrac{\Delta\,[O_2]}{\Delta t}$

Average rate of reaction $= -\dfrac{d\,[N_2O_5]}{2\times dt} = -\dfrac{d\,[NO_2]}{4\times dt} = \dfrac{d\,[O_2]}{dt}$

Units of rate of reaction:–

❑ If concentration is in mol L^{-1} and time is in seconds then the unit of rate is **mol L^{-1} s^{-1}** .

❑ In gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures (atm), then the unit of the rate is **atm s^{-1}** .

Q. The decomposition of N_2O_5 in CCl_4 at 318K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol L^{-1} and after 184 minutes, it is reduced to 2.08 mol L^{-1}. The reaction takes place according to the equation

$$2N_2O_5 \rightarrow 4\ NO_2\ + O_2.$$

Calculate,

(i) The average rate of this reaction.

(ii) The rate of disappearance of N_2O_5

(iii) The rate of production of NO_2 and

(iv) The rate of production of O_2

(v) The average rate in terms of hours and seconds.

Answer

(i)   The average rate of the reaction = 6.79 x 10^{-4} mol L^{-1} min^{-1}

(ii) The rate of disappearance of N_2O_5 = = 1.35 x 10^{-3} mol L^{-1} min^{-1}

(iii) The rate of production of NO_2 and = 2.71 x 10^{-3} mol L^{-1} min^{-1}

(iv) The rate of production of O_2 = 6.79 x 10^{-4} mol L^{-1} min^{-1}

(v) The average rate in terms of hours and seconds

$\qquad$ = 4.074 x 10^{-2} mol L^{-1} hr^{-1}

$\qquad$ = 1.13 x 10^{-5} mol L^{-1} sec^{-1}

Q. Consider the formation of ammonia

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The pressure of hydrogen of this reaction was found to decrease from 20 atm to 8 atm in 100 seconds.

Calculate

(i) The average rate of this reaction.

(ii) The rate of disappearance of N_2

(iii) The rate of disappearance of H_2

(iii) The rate of production of NH_3 and

(v) The average rate in terms of hours

Answer

(i) The average rate of the reaction $= 0.04$ atm sec^{-1}

(ii) The rate of disappearance of $N_2 = 0.04$ atm sec^{-1}

(iii) The rate of disappearance of $H_2 = 0.12$ atm sec^{-1}

(iii) The rate of production of NH_3 and $= 0.08$ atm sec^{-1}

(v) The average rate in terms of hours $= 144$ atm sec^{-1}

Factors affecting the Rate of a Chemical Reaction

1-Nature of reactant

2-Concencentration of Reactants:

Rate of reaction is directly proportional to conc. of reactants
(partial pressure in case of gaseous - phase reactions).

3-Temperature : Rate of reaction increases with increase
in temperature.

4-Presence of Catalyst : A catalyst alters the Rate of a reaction.

5-Surface Area of the Reactants:
Rate of reaction $\propto$ surface area.

Effect of concentration on rate of reaction:

Rate Law (or) Rate expression:

It is a mathematical expression that relates rate of a reaction with rate constant and the concentration of reactants which actually influence the rate.

Consider the reaction aA + bB → Products

Rate law expression for the reaction is

Rate α $[A]^x[B]^y$

Rate $= k\,[A]^x[B]^y$

where x and y are determined experimentally and cannot be deduced from the balanced chemical equation.

k is rate constant or specific reaction rate.

Rate constant is defined as the rate of reaction when the concentrations of all reactants are unity.

Rate Constant (k) :
For a general reaction

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

Rate of reaction = k [A]^x[B]^y
   Where k is known as rate constant
   When [A] = [B] = 1 mol/L, then

Rate of reaction = k

thus rate constant of a chemical reaction may be defined as **the reaction rate when the concentration of each   reactant is unity.**

The value of rate constant is definite and constant for a particular reaction at given temperature

Consider the reaction aA + bB → Products

Rate law expression for the reaction is

$$\text{Rate} = k[A]^x[B]^y$$

Differential rate equation for the reaction:

$$\frac{-d[R]}{a \times dt} = k[A]^x[B]^y$$

Order of a Reaction

The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

For a general reaction

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

Rate law is

Rate = k $[A]^x[B]^y$

Here ,

x = order of reaction w.r.t. A

y = order of reaction w.r.t. B

Overall order of reaction = x + y

➢ **Order of a reaction can be 0, 1, 2, 3 and even a fraction.**

➢ Depending upon order of reaction, reactions are termed as zero, first or second order reactions.

➢ A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

➢ Order of reaction cannot be predicted by merely from the stoichiometry of balanced chemical equation. Order cannot be predicted theoretically but must be determined experimentally.

Order of reaction and Unit of rate constant:

(i) For zero order reaction $\quad$ rate $= k\,[A]^0$

$$k = \text{rate} = \text{mol L}^{-1}\text{sec}^{-1}$$

(Unit of rate constant and rate of reaction are same for zero order reaction)

(ii) For first order reaction $\quad$ rate $= k\,[A]^1$

$$k = \frac{\text{rate}}{[A]} = \frac{\text{mol L}^{-1}\text{sec}^{-1}}{\text{mol L}^{-1}} = \text{sec}^{-1}$$

Unit of rate constant for first order reaction is

sec^{-1} (or) min^{-1} (or) hour^{-1} (or) yr^{-1}

(iii) For second order reaction $\quad$ rate $= k\,[A]^2$

$$k = \frac{\text{rate}}{[A]^2} = \frac{\text{mol L}^{-1}\text{sec}^{-1}}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1}\,\text{sec}^{-1}$$
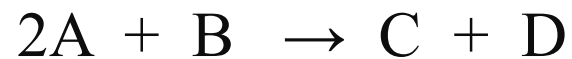
For n^{th} order reaction k has the unit $(\text{mol L}^{-1})^{1-n}\,\text{sec}^{-1}$ (or) $M^{1-n}\,\text{sec}^{-1}$

Q. From the rate expression for the following reaction, determine the order of the reaction and the unit of the rate constants.

$$3NO(g) \rightarrow N_2O\ (g)$$
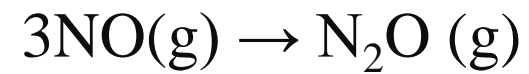
$$\text{Rate} = k[NO]^2$$

Q. Consider a reaction:

$$2A + B \rightarrow C + D$$

The reaction is third order in A and second order in B.

(i) Write the rate law expression.

(ii) Also write the differential rate equation

(iii) How is the rate affected on increasing the concentration of A two times?

(iv) How is the rate affected on increasing the concentration of B three times?

(v) How is the rate affected when the concentrations of both A and B are doubled?

Answer

(i) Rate $= k\,[A]^3[B]^2$
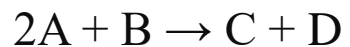
(ii) $\dfrac{-d[A]}{2x\,dt} = k\,[A]^3[B]^2$

(iii) 8 times

(iv) 9 times

(v) 32 times

Q. The rate of a reaction increases 16 times when the concentration of reactant doubles. Calculate the order of the reaction.

Q. The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \rightarrow C + D$$

Experiment	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

Rate $= k\,[A]^x\,[B]^y$

EXP I 6×10^{-3} $= k\,(0.1)^x\,(0.1)^y$ ---- Equation 1

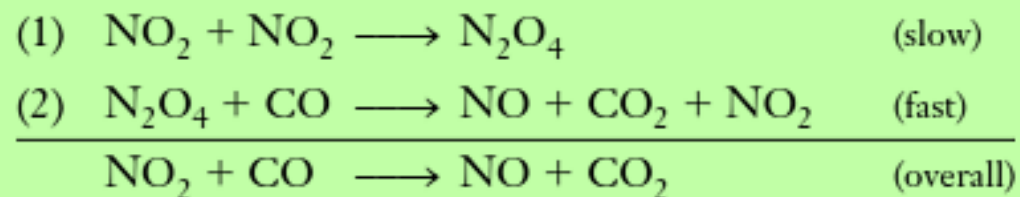EXP IV 2.4×10^{-2} $= k\,(0.4)^x\,(0.1)^y$ ---- Equation 2

On dividing 2/1

     $4 = 4^x$

     Hence x = 1

Elementary & complex reactions

Elementary reactions are those which complete in one step while complex reactions are multistep reactions where products are obtained after completion of a sequence of elementary reactions.

(1)	$NO_2 + NO_2 \longrightarrow N_2O_4$	(slow)
(2)	$N_2O_4 + CO \longrightarrow NO + CO_2 + NO_2$	(fast)
	$NO_2 + CO \longrightarrow NO + CO_2$	(overall)

Molecularity of a Reaction

Molecularity of a reaction is simply the number of reacting species (atoms, ions or molecules) involving is an elementary reaction which must collide simultaneously.
Let us consider the following reactions,

Reaction	Molecularity
(i) $NH_4 NO_2 \longrightarrow N_2 + 2H_2O$	1. (Unimolecular)
(ii) $2HI \longrightarrow H_2 + I_2$	2. (Bimolecular)
(iii) $2NO + O_2 \longrightarrow 2NO_2$	3. (Trimolecular)

Since the chances of collision and reaction of more than three molecules at a time are very less, the molecularity greater than three is rare.

For complex reactions,the molecularity is obtained for individual steps,The individual steps are obtained from the mechanism of the reaction
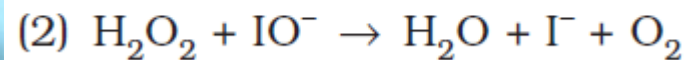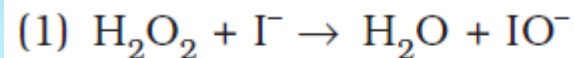
Rate Law and Mechanism

Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$
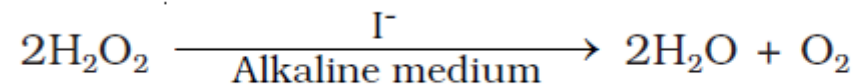
The rate equation for this reaction is found to be

$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

(1) $H_2O_2 + I^- \rightarrow H_2O + IO^-$

(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

For complex reaction, order is given by the slowest step and generally, molecularity of the slowest step is same as the order of the overall reaction

$2NO + O_2 \rightarrow 2NO_2$. The rate law for this reaction is

rate = $K[NO]_2[O_2]$

propose a mechanism for the above reaction

| Order	Molecularity
1.It is the sum of the powers to which the conc: terms are raised in the rate law expression.	1.It is the no: of reacting species involved in simultaneous collision during a reaction.
2. It is determined experimentally	2. It is a theoretical concept
3. Order can be zero	3. Molecularity cannot be zero.
4. It is determined from the slow step in a complex reaction.	4. It can be determined for all step.
5. It explains the mechanism of the reaction.	5.It does not explain the mechanism of the reaction.

Integrated Rate Equations

a) Zero order reaction

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$
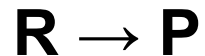
$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k \, dt$$

Integrating both sides between proper limits

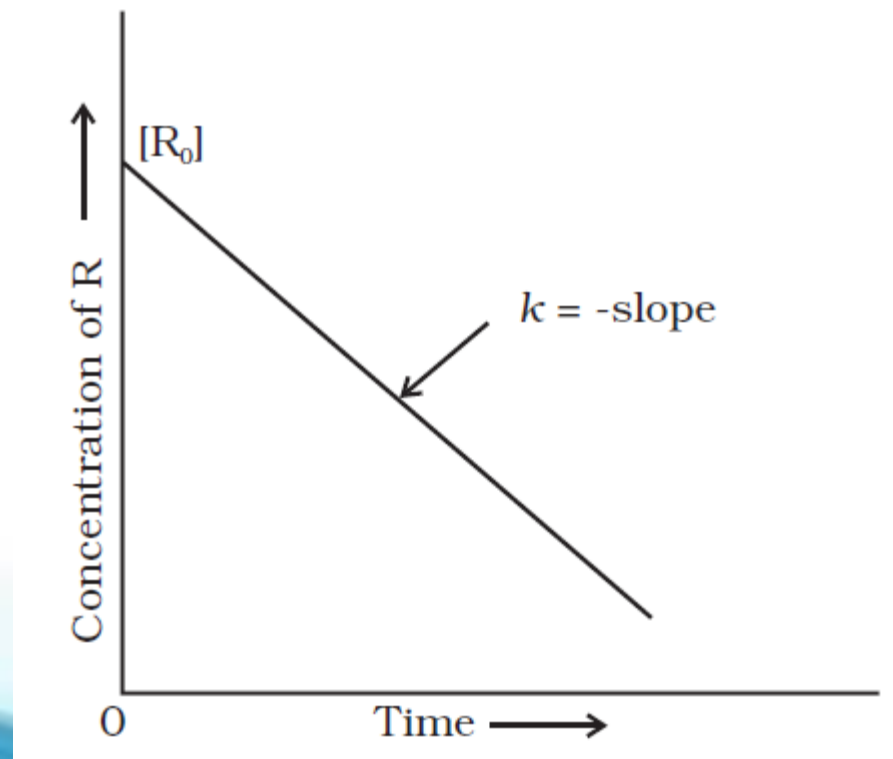$$\int_{R_0}^{R} d[R] = -k \int_{0}^{t} dt$$

$$[R] - [R_o] = -kt$$
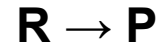
Or

$$[R_o] - [R] = kt$$

Or

$$k = \frac{[Ro] - [R]}{t}$$

First Order Reactions

First order reaction means that the rate of the reaction is proportional to first power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

or $\quad \dfrac{d[R]}{[R]} = -kdt$

Integrating both sides between proper limits

$$\int_{R_0}^{R} \frac{d[R]}{R} = -k \int_0^t dt$$

$$\ln[R] - \ln[R_0] = -kt$$

Or

$$\ln[R_0] - \ln[R] = kt$$

Or

$$kt = \ln \frac{[Ro]}{[R]}$$
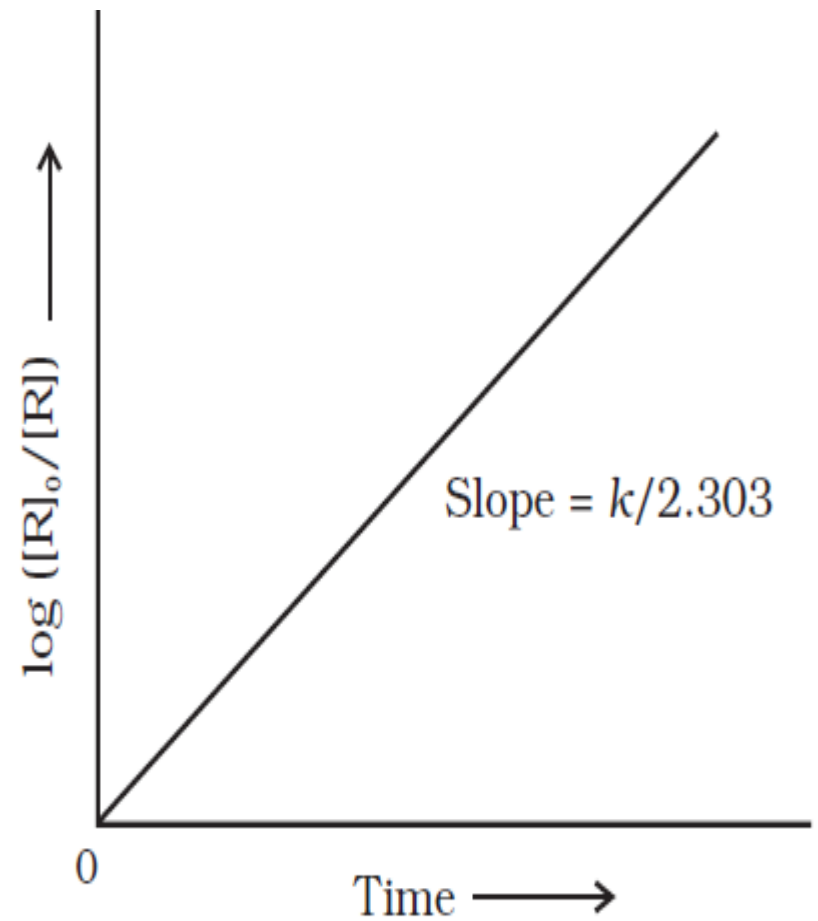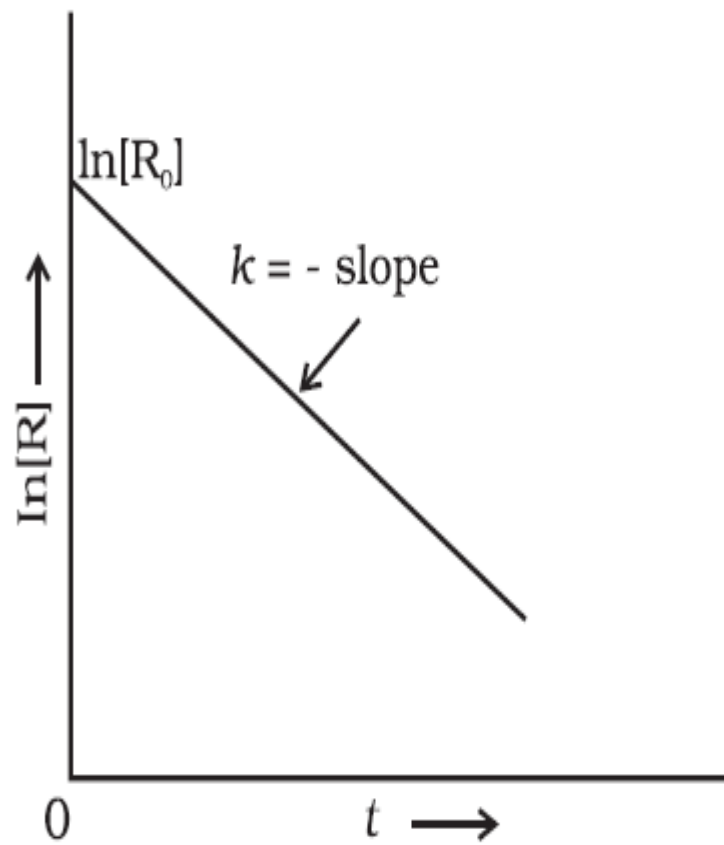
Or

$$k = \frac{1}{t} \ln \frac{[Ro]}{[R]}$$

$$k = \frac{2.303}{t} \log_{10} \frac{[Ro]}{[R]}$$

$$k = \frac{2.303}{t} \log_{10} \frac{[Ro]}{[R]}$$

$$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

Integrated rate expressions in terms of partial pressures (First order gas phase reactions)

consider a typical first order gas phase reaction

A(g) → B(g) + C(g)

Let p_1 be the initial pressure of A and p_t the total pressure at time 't'.
Integrated rate equation for such a reaction can be derived as:

Total pressure $p_t = p_A + p_B + p_C$
If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each

	A(g)	→	B(g)	+	C(g)
At $t = 0$	p_i atm		0 atm		0 atm
At time t	(p_i-x) atm		x atm		x atm

where, p_i is the initial pressure at time $t = 0$.
$p_t = (p_i - x) + x + x = p_i + x$
$x = (p_t - p_i)$
where, Partial pressure A at time t, $p_A = p_i - x = p_i - (p_t - p_i)$
$= 2p_i - p_t$

$$k = \left(\frac{2.303}{t}\right)\left(\log\frac{p_i}{p_A}\right)$$

$$= \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$

$t_{1/2}$ for a Zero Order Reactions

For a zero order reaction, rate constant is given by equation

$$k = \frac{[R]_0 - [R]}{t}$$

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

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

Half-Life of a Reaction

For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

at $t_{1/2}$ $[R] = \frac{[R]_0}{2}$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]/2}$$

or $t_{1/2} = \frac{2.303}{k} \log 2$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k}$$

Pseudo - first order reaction

Reactions which are not truly of the first order but under certain conditions reactions become that of first order are called pseudo unimolecular reaction.

For example: Hydrolysis of ester in presence of acid

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

From this reaction, the rate expression should be

$$r = k [ester] [H_2O]$$

Since, hydrolysis takes place in the excess of H_2O and concentration change of H_2O is negligible practically.

therefore, $r = k' [ester]$

Where $k' = k[H_2O]$.

Q 1:The decomposition of NH_3 on platinum surface $2NH_3 \rightarrow N_2 +3H_2$ is a zero order reaction with k=2.5x10^{-4} molL^{-1}S^{-1}·What are the rates of production of N_2 and H_2?

Q2:A reaction is second order in A and first order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected
a)on increasing the concentration of A three times?
b)when the concentration of both A and B are doubled?

Q3:A reaction is of second order with respect to its reactant. How will its reaction rate be affected
if the concentration of the reactant is
(i) doubled
(ii) reduced to half ?

Q4:The data given below is for the reaction, $2N_2O_5 (g)$ $\rightarrow 4NO_2 (g) + O_2 (g)$ at 298 K

S. No.	$[N_2O_5]$ (mol L^{-1})	Rate of disappearance of N_2O_5(mol L^{-1} min^{-1})
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine for this reaction :
(i) order of reaction
(ii) rate constant
(iii) rate law.

Q5: For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Q6:In a first order reaction, the concentration of the reactant is reduced from 0.6 mol L^{-1} to 0.2 mol L^{-1} in 5 minutes. Calculate the rate constant of the reaction.

Q7:A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value.

Q8:The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at constant volume:
$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$. Calculate the rate constant

Experiment	Time/s	Total pressure/atm
1	0	0.4
2	100	0.7

Q9:The half-life for decay of radioactive $_{14}C$ is 5730 years. An archaeological artifact containing wood has only 80% of the $_{14}C$ activity as found in living trees. Calculate the age of the artifact.

Q10:A first order reaction has a rate constant value of 0.00510 min^{-1}. If we begin with 0.10 M concentration of the reactant, how much of the reactant will remain aer 3.0 hours?