Chemical kinetics

Rate of a chemical Rxn:—

It is defined as the amount of change in concentration divided by the corresponding time interval.

$$\frac{\Delta x}{\Delta t} = \frac{dx}{dt} = \frac{x_1 - x_2}{t_2 - t_1}$$

where, Δx or dx is the concentration change $(x_1 - x_2)$ in the time interval Δt or dt $(t_2 - t_1)$

- concentration is generally expressed in active mass, i.e, $mol L^{-1}$.

$$\text{Reactant } (R) \longrightarrow \text{product } (P)$$

$$-\frac{\Delta [R]}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

For the reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\frac{dx}{dt} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Law of Mass action:—

The rate at which a substance reacts is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances.

$$\textcircled{A} + B \longrightarrow C + D$$

$$-\frac{d[A]}{dt} \propto [A] \text{ and } -\frac{d[B]}{dt} \propto [B]$$

so, that rate of the rxn,

$$\frac{dx}{dt} \propto [A][B]$$

$$\frac{dx}{dt} = k[A][B]$$

k = rate constant
[A] and [B] are active masses or molar concentration of the reactants A and B.

- At a time when, $[A] = [B] = 1 \text{ mol } L^{-1}$.

$$\frac{dx}{dt} = k$$

▨ Rate law, Molecularity and Order of Reaction:—

Total number of molecules of the reactants involved in the reaction as shown by chemical equation is termed its molecularity. It is always an integral value and is never zero.

$$A + 2B \longrightarrow \text{product}$$

Note:— QD.
For elementary rxn:—
Order = molecularity

Rate, $\frac{dx}{dt} = k[A]^x[B]^y$

the above equation is called rate law.

$x + y \Rightarrow$ overall order of a rxn
whereas x and y represent the order w.r.t the reactants A and B respectively.

order of a reaction can be 0, 1, 2, 3 and even a fraction.

① Rate of a reaction A → product increases 2.25 times when the concentration of reactant increases 1.5 times, what is the order of the rxn?

$$\dot{A} \longrightarrow \text{product}$$

$$r = k[A]^{\alpha} \quad \text{—— ①}$$

$$[2.25]r = k[1.5A]^{\alpha} \quad \text{—— ②}$$

$$② \div ① \Rightarrow \quad \frac{2.25\cancel{r}}{\cancel{r}} = \frac{\cancel{k}[1.5A]^{\alpha}}{\cancel{k}[A]^{\alpha}}$$

$$2.25 = [1.5]^{\alpha}$$

$$[1.5]^2 = [1.5]^{\alpha}$$

$$\therefore \alpha = 2$$

Hence second order reaction.

Q.
② At 1100K, the following data obtained by homogeneous reaction

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

$[NO]$	$[H_2]$	Rate
5×10^{-3}	2.5×10^{-3}	3×10^{-5}
15×10^{-3}	2.5×10^{-3}	9×10^{-5}
15×10^{-3}	10×10^{-3}	36×10^{-5}

Calculate the order w.r.t NO, H_2 and overall rxn.

Ans:— $r = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{1}{2}\frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[H}{dt}$

$$r = k[NO]^{\alpha}[H_2]^{\beta} \quad \text{—— ①}$$

$$3\times10^{-5} = [5\times10^{-3}]^{\alpha}[2.5\times10^{-3}]^{\beta} \text{———} ①$$

$$9\times10^{-5} = [15\times10^{-3}]^{\alpha}[2.5\times10^{-3}]^{\beta} \text{———} ②$$

$$36\times10^{-5} = [15\times10^{-3}]^{\alpha}[10\times10^{-3}]^{\beta} \text{———} ③$$

$$③ \div ② \Rightarrow \left[\frac{10\times\cancel{10^{-3}}}{2.5\times\cancel{10^{-3}}}\right]^{\beta} = \frac{\overset{4}{\cancel{36}}\times\cancel{10^{-5}}}{\cancel{9}\times\cancel{10^{-5}}}$$

$$4^{\beta} = 4^{1}$$

$$\therefore \beta = 1$$

The order w.r.t H_2 is first order.

$$② \div ① \Rightarrow \left[\frac{\overset{3}{\cancel{15}}\times\cancel{10^{-3}}}{\cancel{5}\times\cancel{10^{-3}}}\right]^{\alpha} = \frac{\overset{3}{\cancel{9}}\times\cancel{10^{-5}}}{\cancel{3}\times\cancel{10^{-5}}}$$

$$3^{\alpha} = 3$$

$$\therefore \alpha = 1$$

$$r = k[NO]^{1}[H_2]^{1}$$

order w.r.t NO is first order.

overall order ~~and~~ of the rxn is $= 2$

$\alpha + \beta$

$1 + 1$

$= 2$

▨ Zero order reaction :-

$$A \longrightarrow \text{product}$$

$$-\frac{d[A]}{dt} = k[A]^0$$

$$-d[A] = k \cdot dt$$

$$\int_{[A]_0}^{[A]} d[A] = -k\int_0^t dt$$

$$[A]-[A]_0 = -kt$$

$$\boxed{[A] = [A]_0 - kt}$$

▨ Alternative method :-

$$A \longrightarrow \text{product}$$

	A	product
At, $t=0$	a	0
$t=t$	$a-x$	x

$$\frac{dx}{dt} = k_0[A]^0 = k_0$$

$$dx = k_0\,dt$$

$$\therefore \boxed{x = k_0 t}$$

$$[A] = [A_0] - kt$$

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

If concentration of the product is x_1 at time t_1 and x_2 at time t_2, then,

$$k = \frac{x_1 - x_2}{t_1 - t_2}$$

characteristics:-

① Half-life-period:-

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

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

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

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

$$t_{1/2} \propto [A]_0$$

$t = t_{1/2}$, $x = \frac{a}{2}$

$$\therefore \boxed{t_{1/2} = \frac{a}{2k}}$$

$$\boxed{t_{1/2} \propto a}$$

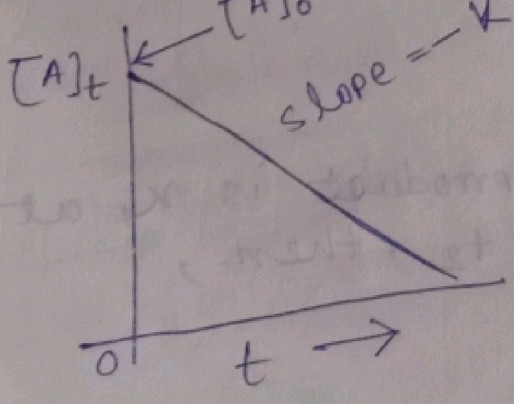
$$\boxed{t_{1/2} \propto \frac{1}{k}}$$

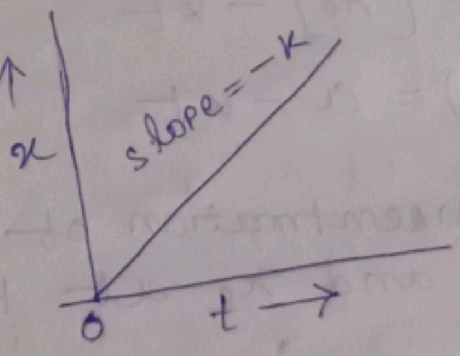
At, $t = t_{3/4}$, $x = \frac{3a}{4}$

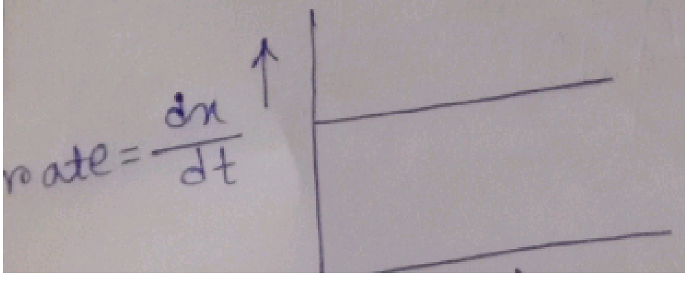
$$\therefore t_{3/4} = \frac{3a}{4k} = \frac{3}{2}\,\frac{a}{2k} = \frac{3}{2}\,t_{1/2}$$

$$\therefore \boxed{t_{3/4} = 1.5\,t_{1/2}}$$

② Graphs:-







Example:-

Photochemical rxns ($H_2 + Cl_2 \longrightarrow 2HCl$) and decomposition of various gases on the surface of metallic catalyst such as decomposition of HI on gold surface is exhibits zero order kinetics. Zero order rxns generally take place in a heterogeneous system.

$$H_2C=CH_2\,(g) + H_2\,(g) \xrightarrow{Ni(s)} CH_3-CH_3\,(g)$$

③ unit of rate constant:-

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

$\therefore\ k = mol^{1-n} L^{n-1} s^{-1}$

$n = 0$ (for zero order rxn)

$k = mol^1 L^{-1} s^{-1}$

$\therefore\ \boxed{k = mol\ lit^{-1} s^{-1}}$

④ completion time:-

when, $t = t_{comp}$, $[A] = 0$

$\therefore\ [A]_0 = k\,t_{complete}$

$\therefore\ \boxed{t_{comp} = \frac{[A]_0}{k}} =$ finite time

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

$\therefore\ t_{1/2} = \frac{1}{2} t_{comp}$

$\therefore\ \boxed{t_{comp} = 2t_{1/2}}$

④ Zero order reaction must be multistep!-

For an elementary rxn, order and molecularity must be same. since molecularity of an elementary rxn is 1, therefore minimum order of an elementary rxn must be 1 and can't be equal to zero.

So, zero order rxn is multistep

▨ First Order Reaction :-

$$A \longrightarrow \text{product}$$

$$-\frac{d[A]}{dt} = k[A]^1$$

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

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k\int_0^t dt$$

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

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$\therefore \boxed{[A] = [A]_0\, e^{-kt}}$$

$$\boxed{k = -\frac{1}{t}\ln\frac{[A]}{[A]_0}}$$

Alternative method:—

$$A \longrightarrow \text{product}$$

$t=0$ $\quad a \quad 0$

$t=t$ $\quad (a-x) \quad x$

Rate of formation of Product —

$$\frac{dx}{dt} = k(a-x)^1$$

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

$$\ln(a-x)(-1) = kt + z$$

$$-\ln(a-x) = kt + z$$

when, $t=0$, $x=0$; $z = -\ln a$

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

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

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

$$\boxed{kt = \ln\frac{a}{a-x}}$$

$$\boxed{k = \frac{1}{t}\ln\frac{a}{a-x}}$$

$$\boxed{k = \frac{2.303}{t}\log\frac{a}{a-x}}$$

$$\boxed{\log\frac{c}{c_0} = -kt}$$

The reaction where rate is directly proportional to the reactant concentration is known as 'first order rxn'.

Characteristics:—

① Half-life period:—

$$t = \frac{1}{k} \ln \frac{a}{a-x}$$

when, $t = t_{1/2}$; $x = \frac{a}{2}$

$$t_{1/2} = \frac{1}{k} \ln \frac{a}{a - a/2}$$

$$t_{1/2} = \frac{1}{k} \ln \left(\frac{2a}{a}\right)$$

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

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

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

when, $t = t_{3/4}$; $x = \frac{3a}{4}$

$$t_{3/4} = \frac{1}{k} \ln \frac{a}{a - \frac{3a}{4}}$$

$$t_{3/4} = \frac{1}{k} \ln \frac{4\cancel{a}}{\cancel{a}}$$

$$t_{3/4} = \frac{1}{k} \ln 2^2$$

$$t_{3/4} = \frac{2}{k} \ln 2$$

$$t_{3/4} = \frac{2}{k} \times 0.693$$

$$\boxed{t_{3/4} = 2 t_{1/2}}$$

75% complete = 2 × 50% complete.

② unit of rate constant :—

$k = mol^{1-n} lit^{n-1} s^{-1}$

$n = 1$ (for first order rxn)

$k = mol^{1-1} lit^{1-1} s^{-1}$

∴ $\boxed{k = s^{-1}}$

③ Time of completion :—

when, $t = t_{comp}$; $[A] = 0$

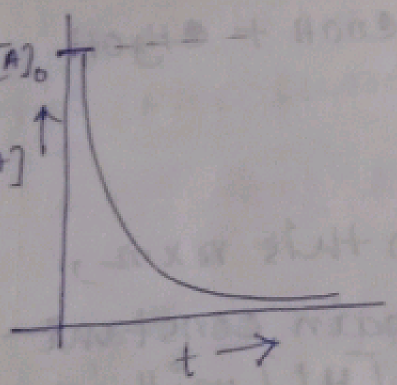
∴ $[A] = [A]_0 e^{-kt}$

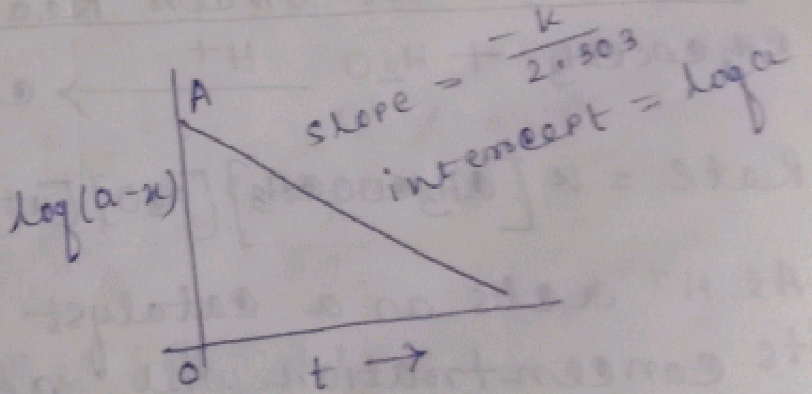
when, $t = \infty$, $[A] = 0$

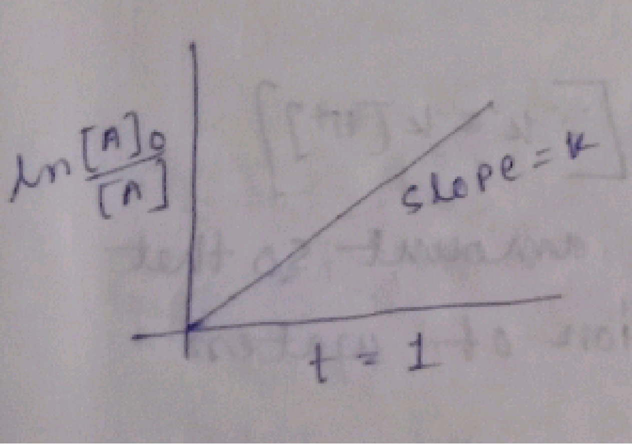
First order reaction takes infinite time to complete.

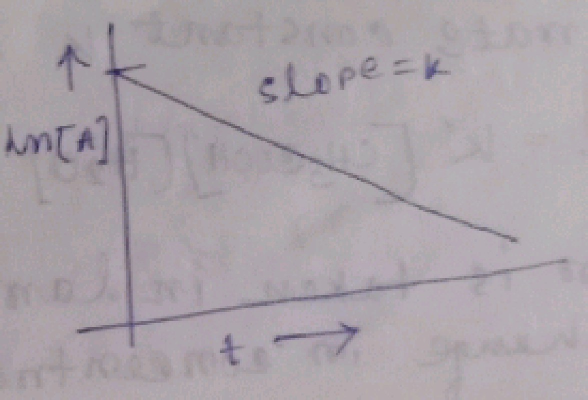
First order rxn is never be completed in a finite time.

④ Graphs :—









Examples:-

following are some examples of first order rxns ——

(i) $H_2O_2(S) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

(ii) $2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$

(iii) $(CH_3)_3CCl + OH^-(aq) \longrightarrow (CH_3)_3COH + Cl^-(aq)$

Note:-

- All radioactive decays are first order rxns.
- $t_{av} = \frac{1}{k_1} = \frac{t_{1/2}}{0.693} = 1.443t_{1/2}$
- ~~During one~~ t_{av} is sometimes referred to as the natural life time of reactant A.

Pseudo First order Reaction:-

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

$$Rate = k[CH_3COOCH_3][H_2O][H^+]$$

As H^+ acts as a catalyst in this rxn, its concentration will remain constant with time. so we can include $[H^+]$ within the rate constant k.

$$Rate = k'[CH_3COOH](H_2O) \quad [\because k' = k[H^+]]$$

water is taken in large amount so that the change in concentration of water

---

is negligi
Ra

∴ The
order o
the ab
order
as pse

Q
① Nitro
the r
gaseou
devel
a fun
press
Ans:-

t=0

t=t

tot

is negligible during the rxn.

$$Rate = k'' [CH_3COOCH_3]$$

∴ The rxn is actually a second order or third order rxn, but under the above conditions, it becomes a first order rxn. This type of rxn is known as pseudo first order rxn.

Q ① Nitrous oxide decomposses into N_2 and O_2, the reactant and product being all gaseous. If the reaction is first order, develope expression for rate constant as a function of time, initial pressure and total pressure.

Ans:- $N_2O(g) \longrightarrow N_2(g) + \frac{1}{2}O_2(g)$

$t=0$	P_i	0	0
$t=t$	$(P_i - x)$	x	$\frac{x}{2}$

total pressure $P = P_i - \cancel{x} + \cancel{x} + \frac{x}{2}$

$$P = P_i + \frac{x}{2}$$

$$P = \frac{2P_i + x}{2}$$

$$\therefore 2P - 2P_i = x$$

$$\therefore x = 2(P - P_i)$$

$$P_{NO_2} = P_i - x = P_i - 2(P - P_i)$$

$$= P_i - 2P + 2P_i$$

$$P_{NO_2} = 3P_i - 2P$$