

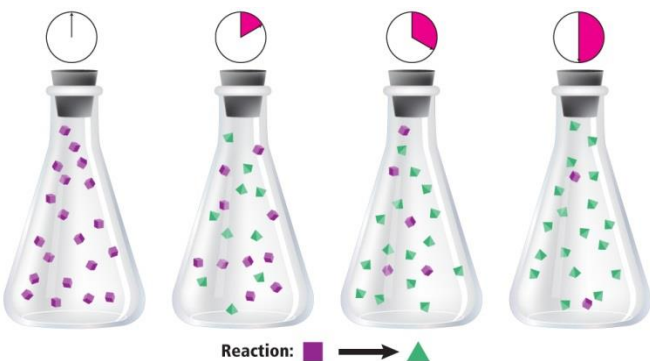
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In the name of
Allah





Physical chemistry– M.SC.



Lecture No. 7

Kinetic chemistry

6-12-2015

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Thermodynamics – does a reaction take place?

Thermodynamics of chemical processes

Chemical thermodynamics describe the energetic balance of chemical processes. This tells us which processes can principally occur and whether they consume or release energy.

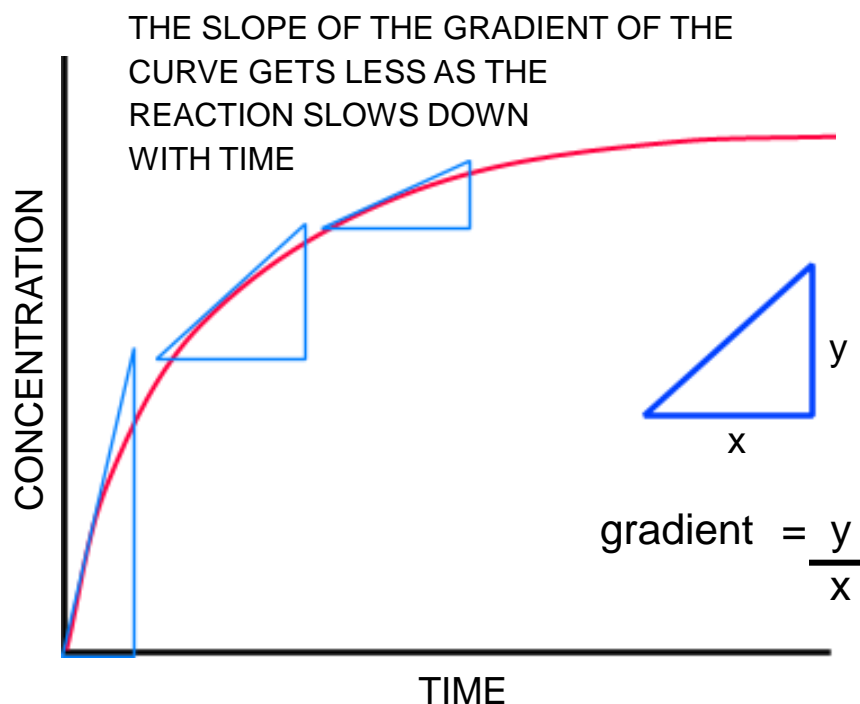
Kinetics – how fast does a reaction proceed?

Kinetics of chemical processes

Reaction kinetics describe at which rate chemical reactions occur.

MEASURING THE RATE

RATE How much concentration changes with time. It is the equivalent of velocity.



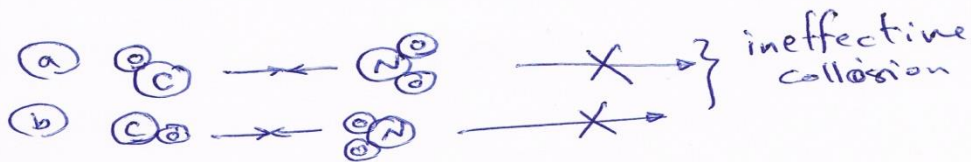
- the rate of change of concentration is found from the slope (gradient) of the curve
- the slope at the start of the reaction will give the **INITIAL RATE**
- the slope gets less (showing the rate is slowing down) as the reaction proceeds

So, the Higher order reactions are rare, that beyond to energy barrier & orientation which caused the chemical reaction.

To make effective collision (reaction) must produce the reaction with sufficient energy $E \geq E_{Th}$, to break the chemical bonds in the reactant molecules.

* E_{Th} is threshold energy.

If molecules have a sufficient energy, but not all molecules will undergo effective collision, that depended on the proper orientation.



Effective collision

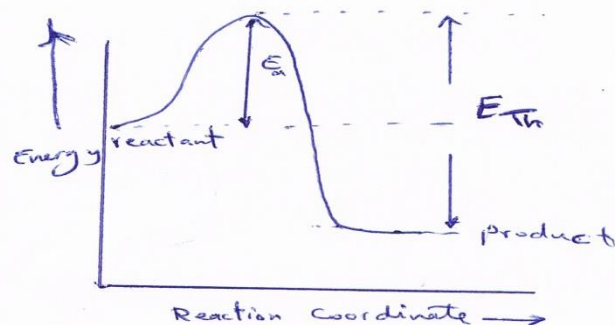


Fig (5): The energy of reaction.

Chemical Kinetics

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).

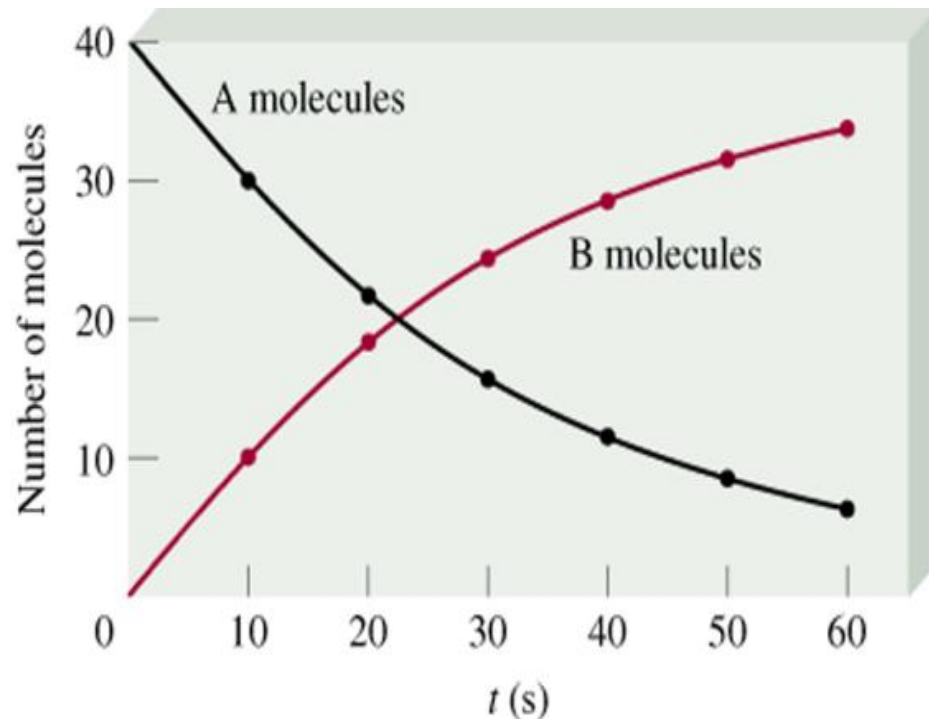


$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt



Because $[A]$ decreases with time, $\Delta[A]$ is negative.

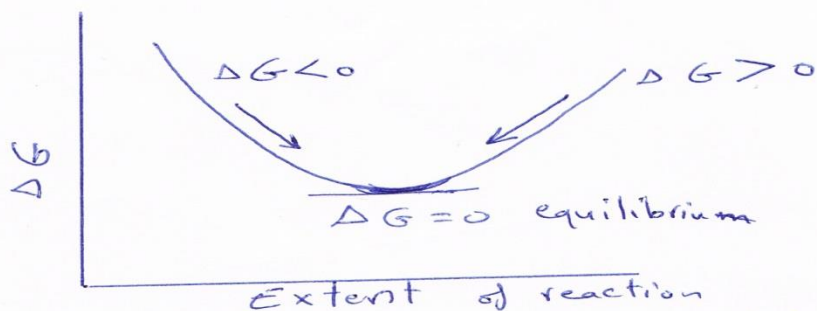
(3)

- There are good two questions;

First: Where is chemical reaction going?

Second: How fast is getting there?

The answer of first question is determined by equilibrium, because an reaction may be taken high velocity at beginning then arrived to equilibrium, equilibrium is happen when chemical potential of reactants are equal to the chemical potential of products, as in Fig. 4:



Fig(4) Explain the equilibrium state for reaction.

Order and Molecularity of Reaction

order of reaction is defined as "the sum of the powers of concentration term in the experimentally established rate equation".



(4)

$$\text{Theoretical Rate} = k [A]^{\alpha} [B]^{\beta} \quad \text{----- (3)}$$

$$\text{Experimental Rate} = k [A]^{\alpha} [B]^{\beta} \quad \text{----- (4)}$$

where: k is rate constant.

$$\boxed{\text{Order} = \alpha + \beta} \quad \text{----- (5)}$$

Hence, the order of reaction defined as "the number of molecules whose concentration change during the reaction at a given temperature".

The order of reaction isn't more than three, because by depending on the transition theory, it is two substances are attained actually in the chemical reaction.



The suggested orders are

$$\begin{array}{ll} \alpha = 2, \beta = 1 & \longrightarrow \text{Order} = 3 \\ \alpha = 1, \beta = 2 & \longrightarrow \text{Order} = 3 \end{array} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{or less}$$

So, orders of reaction are 1 or 2 or 3.

Molecularity of a reaction is defined as the total number of molecules, in the step leading to the chemical reaction".

⑤

"Molecularity is a theoretical concept and is related to the mechanism of a reaction".

* The molecularity of reaction or stoichiometric is attained from general equation but the order of reaction found experimentally.

* The difference between order & Molecularity for any reaction may be explained in Table (1).

Order	Molecularity
① It is an experimental concept.	① It is theoretical concept.
② It can be fraction, Zero, or negative.	② It can never be fraction, Zero or negative, It is positive only.
③ It can't be determined from balanced or stoichiometric equation.	③ It can be obtained from balanced equation of a single reaction.
④ In case of complex reaction, order is determined by the slowest step of the reaction, rate-determining step	④ In case of complex reaction, molecularity has no significance for complex.

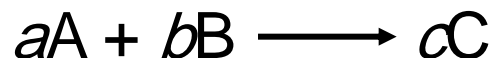


Molecularity = 3 ($\text{CH}_3\text{COOC}_2\text{H}_5, \text{H}_2\text{O}, \text{H}^+$)

order = 1 ($\text{CH}_3\text{COOC}_2\text{H}_5$) So $\begin{cases} \text{H}_2\text{O} = \text{solvent} \\ \text{H}^+ = \text{Catalyst} \end{cases}$ are not calculated.

The Rate Law

The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

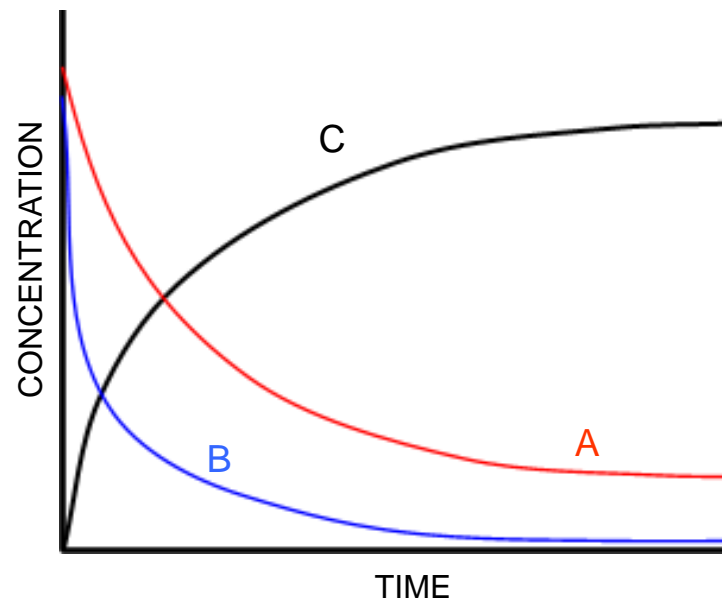


$$\text{Rate} = k [A]^x [B]^y$$

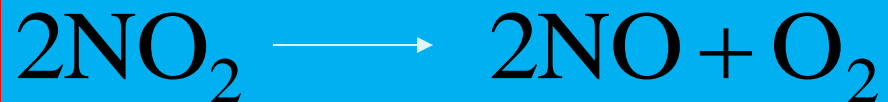
reaction is **xth order** in A

reaction is **yth order** in B

reaction is **(x + y)th order overall**



Initial Rates, NO₂ decomposition



$$\text{rate} = - \frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$$

Experiment	Initial Conc. [NO ₂]	Rate [O ₂] Formation
1	0.01	7.1 x 10 ⁻⁵
2	0.02	2.8 x 10 ⁻⁴

Order of Reaction

► General:

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{-k_2[\text{NO}_2]^n}{-k_1[\text{NO}_2]^n}$$

► Substituting:

$$\frac{2.8 \times 10^{-4}}{7.1 \times 10^{-5}} = \frac{-k_2[0.020]^n}{-k_1[0.010]^n}$$

► Solution:

$$4 = (2)^n \quad \text{so} \quad n = 2$$
$$(\ln 4 = n \ln 2)$$

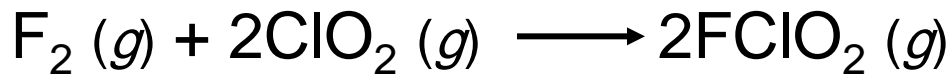


Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

	$[\text{F}_2](M)$	$[\text{ClO}_2](M)$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

$$\text{rate} = k [\text{F}_2]^x [\text{ClO}_2]^y$$

Double $[\text{F}_2]$ with $[\text{ClO}_2]$ constant

Rate doubles $x = 1$

Quadruple $[\text{ClO}_2]$ with $[\text{F}_2]$ constant

Rate quadruples $y = 1$

$$\text{rate} = k [\text{F}_2][\text{ClO}_2]$$

overall order of the reaction = $1 + 1 = 2$

Run #	Initial [A] ([A] ₀)	Initial [B] ([B] ₀)	Initial Rate (v ₀)
1	1.00 M	1.00 M	1.25 × 10 ⁻² M/s
2	1.00 M	2.00 M	2.5 × 10 ⁻² M/s
3	2.00 M	2.00 M	2.5 × 10 ⁻² M/s

What is the order with respect to A? 0

What is the order with respect to B? 1

What is the overall order of the reaction? 1



Determine the rate law and calculate the rate constant for the following reaction from the following data:



Experiment	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}]^x [\text{I}^-]^y$$

$$y = 1$$

$$x = 1$$

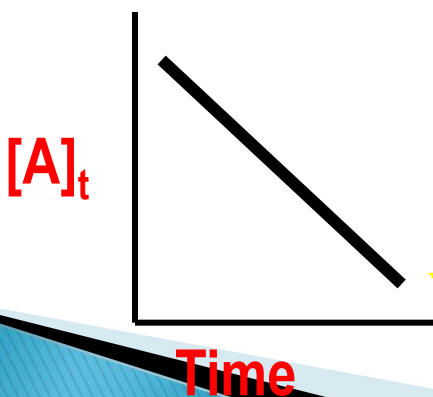
$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

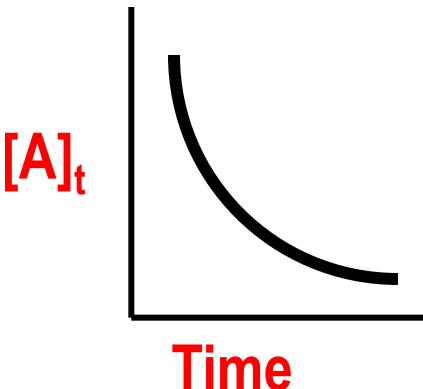
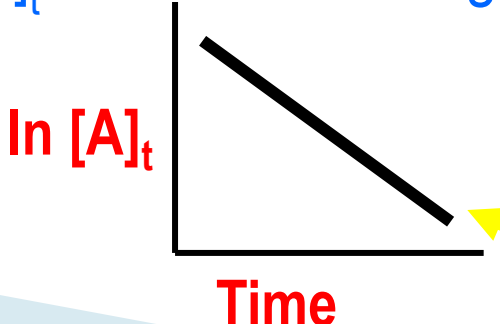
Double $[\text{I}^-]$, rate doubles (experiment 1 & 2)

Double $[\text{S}_2\text{O}_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} = \frac{2.2 \times 10^{-4} \text{ M/s}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08/\text{M}\cdot\text{s}$$

Figure 1: Comparison of reaction orders based on the generic reaction: $A \rightarrow C$.

Rxn order	Rate law (simple format)	Rate law (relating $[A]$ to $[A_0]$)	Units of rate constant (k)
Zero order	$\text{Rate} = -\frac{\Delta[A]}{\Delta t}$ $\text{Rate} = k[A]^0$ $\text{Rate} = k$ 	$-\frac{d[A]}{dt} = k$ $d[A] = -k dt$ $\int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt$ $[A]_t - [A]_0 = -k(t - 0)$ $[A]_t = -kt + [A]_0$	$[A]_t = -kt + [A]_0$ $(M) = -(k)(s) + (M)$ <p>therefore</p> $(k)(s) = (M)$ <p>so</p> $(k) = M/s$ <p>or</p> $(k) = \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

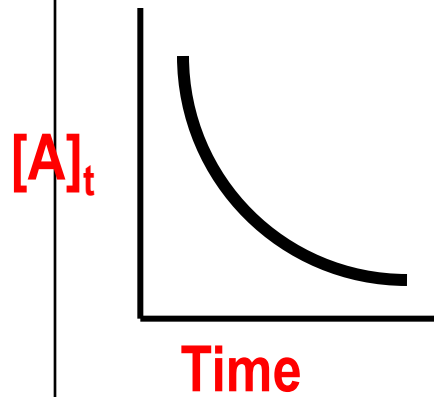
Rxn order	Rate law (simple format)	Rate law (relating [A] to [A] ₀)	Units of rate constant (k)
1 st order	$\text{Rate} = -\frac{\Delta[A]}{\Delta t}$ $\text{Rate} = k[A]^1$ 	$-\frac{d[A]}{dt} = k[A]$ $\frac{d[A]}{[A]} = -k dt$ $\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$ $\ln[A]_t - \ln[A]_0 = -k(t - 0)$ $\ln[A]_t = -kt + \ln[A]_0$ $\log[A]_t = -kt / 2.303 + \log[A]_0$ 	$\ln[A]_t = -kt + \ln[A]_0$ $\text{---} = -(k)(s) + \text{---}$ <p>therefore</p> $(k)(s) = \text{---}$ <p>so</p> $(k) = 1/s$ <p>or</p> $(k) = s^{-1}$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Rate} = k[A]^2$$

(or = $k[A][B]$)

2nd
order



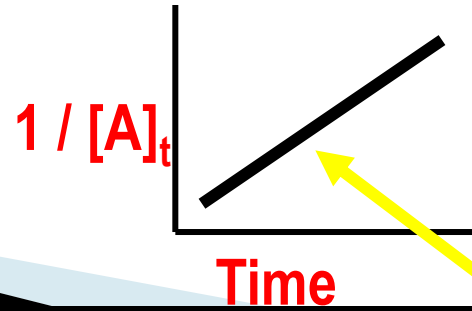
$$-\frac{d[A]}{dt} = k[A]^2$$

$$\frac{d[A]}{[A]^2} = -k dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$-\frac{1}{[A]_t} - \left(-\frac{1}{[A]_0} \right) = -k(t - 0)$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$



$$1/[A]_t = kt + 1/[A]_0$$

$$(1/M) = (k)(s) + (1/M)$$

therefore

$$(k)(s) = (1/M)$$

so

$$(k) = 1/(M \cdot s)$$

or

$$(k) = \text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$$

$$(k) = M^{-1} \cdot s^{-1}$$

7

Zero Order Reaction :

"If the rate of reaction is independent on concentration of reaction, then it is known as Zero order reaction"

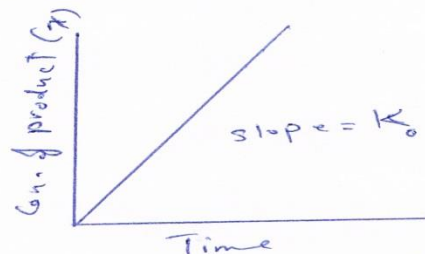
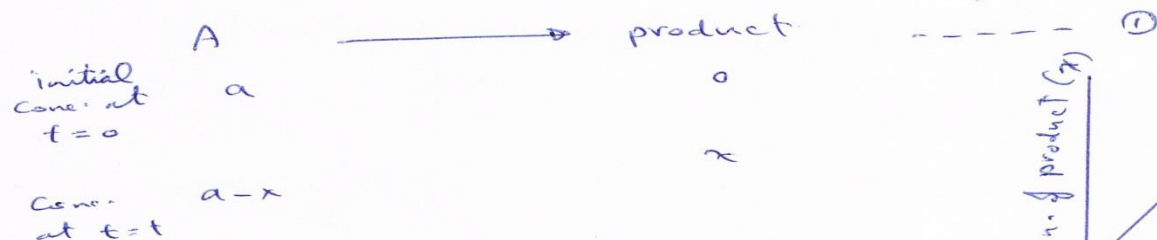


Fig 1: The relation between Conc. & t. for Zero order react.

$$\frac{dx}{dt} \propto (a-x)^0 \quad \text{----- (2)}$$

$$\frac{dx}{dt} = k_0 (a-x)^0 = k_0 \quad \text{---- (3)}$$

k_0 = Rate constant for a Zero order reaction.

On integration :

$$\int_0^x dx = \int_0^t k_0 dt \quad \text{----- (4)}$$

$$\int_0^x dx = k_0 \int_0^t dt \quad \text{----- (5)}$$

$$\therefore x = k_0 t + C \quad \text{----- (6)}$$

where C = constant of integration

if $x=0$ & $t=0$ and substituted in eq. (6)

$$\therefore 0 = k_0 \times 0 + C \longrightarrow \boxed{C=0} \quad \text{---- (7)}$$

$$\boxed{x = k_0 t} \quad \text{0th order reaction eq.} \quad \text{--- (8)}$$

(8)

Unit of Zero Order reaction

$$k_0 = \frac{\text{Conc.}}{\text{Time}} = \frac{\text{mol/L}}{\text{s}} \quad \text{----- (9)}$$

$$\therefore \boxed{k_0 \text{ unit} = \text{mol L}^{-1} \text{s}^{-1}} \quad \text{----- (10)}$$

Half time period: "The time during which half of the reactant changes into product is known as half life period".

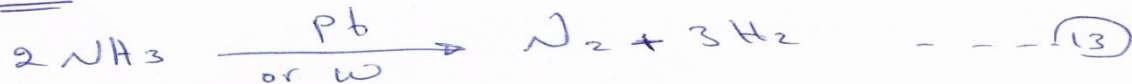
$$t_{1/2} \text{ or } t_{0.5} \quad \text{and} \quad x = \frac{1}{2} a$$

$$k_0 = \frac{a}{2 t_{1/2}} \quad \text{----- (11)}$$

$$\therefore \boxed{t_{0.5} = t_{1/2} = \frac{a}{2 k_0}} \quad \text{----- (12)}$$

In Zero order reaction, the time of half time depends on the initial concentration,

Ex.



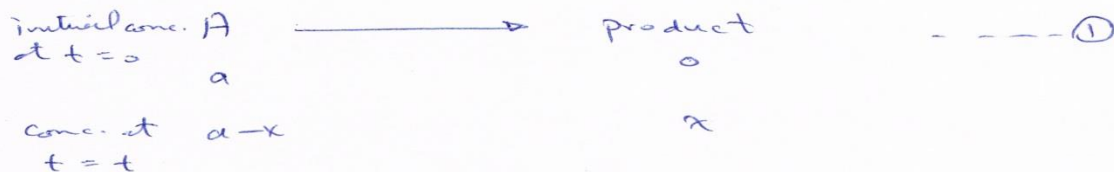
$$\frac{dx}{dt} = k_0 [\text{NH}_3]^0 \quad \text{----- (14)}$$

\therefore Order = Zero

⑨

First Order Reaction :

"If the sum of the power of concentration term in the experimentally established rate equation is one, then it is known as a first order reaction".



$$\frac{dx}{dt} \propto (a-x)^1 \quad \text{--- (2)}$$

Where: k_1 is rate constant for 1st order reaction

$$\therefore \frac{dx}{(a-x)} = k_1 dt \quad \text{--- (3)}$$

On integration:

$$\int_0^x \frac{dx}{(a-x)} = k_1 \int_0^t dt \quad \text{--- (4)}$$

$$\therefore -\ln(a-x) = k_1 t + C \quad \text{--- (5)}$$

$$\text{if } t=0, x=0$$

$$\therefore \boxed{-\ln a = C} \quad \text{--- (6)}$$

substituted by eq. (5)

$$\therefore -\ln(a-x) = k_1 t - \ln a \quad \text{--- (7)}$$

$$\therefore k_1 t = \ln a - \ln(a-x)$$

$$\therefore \boxed{k_1 = \frac{1}{t} \ln \frac{a}{a-x}} \quad \text{--- (8)}$$

(10) or $k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$ ----- (9)

Unit of k_1

$k_1 = \frac{\text{Conc.}}{\text{time} \cdot \text{Conc.}} = (\text{Time})^{-1}$ ----- (10)

or

Unit = $(\text{Conc.})^{1-n} \cdot \text{Time}^{-1}$ ----- (11)

$= (\text{Conc.})^{1-1} \cdot \text{Time}^{-1}$ ----- (12)

Unit of $k_1 = (\text{Time})^{-1}$ ----- (13)

Half time period:

$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$ ----- (14)

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

$\therefore k_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}}$ ----- (15)

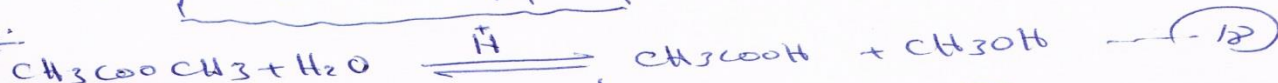
$= \frac{2.303}{t_{1/2}} \log 2$ ----- (16)

$\therefore t_{1/2} = \frac{0.693}{k_1}$ ----- (17)

$\left\{ \begin{aligned} a - \frac{a}{2} \\ = \frac{2a-a}{2} \\ = \frac{a}{2} \end{aligned} \right.$

Half time isn't depended on Conc. (or).

ex:



$\frac{dx}{dt} = k_1 [\text{CH}_3\text{COOCH}_3]$ ----- (19)

$\therefore \text{order} = 1$

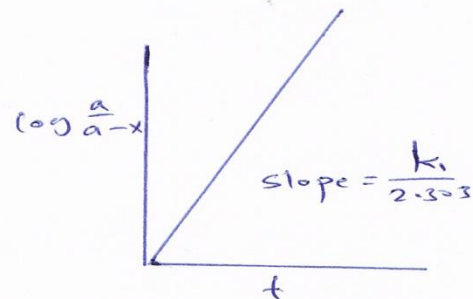


Fig 1: The relation between $\log \frac{a}{a-x}$ & t for 1st order reaction

(11)

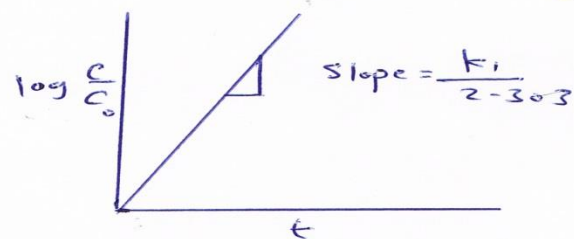
The laws of Rate of reaction can be written, according to types of used techniques:-

→ By using concentration

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k_1 = \frac{2.303}{t} \log \frac{C}{C_0}$$

C_0, C are initial conc. & conc. respectively.



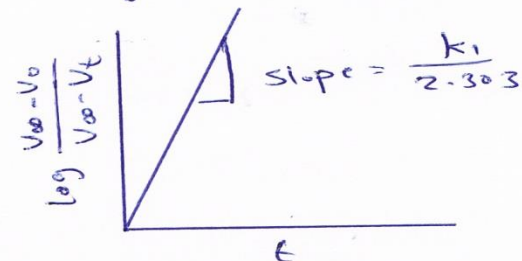
→ By using volume (Titration)

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

V_0 = is volume at $t=0$

V_t = is volume at $t=t$

V_∞ = is volume at infinity time



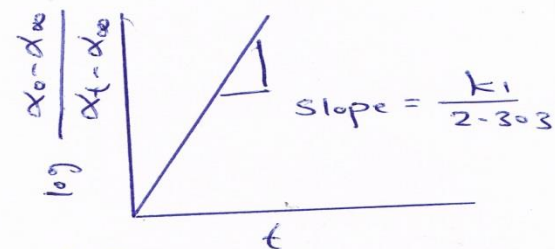
→ By using the polarimetry

$$k_1 = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

α_0 rotation angle at $t=0$

α_t rotation angle at $t=t$

α_∞ rotation angle at infinity time



→ By using the electric conductivity

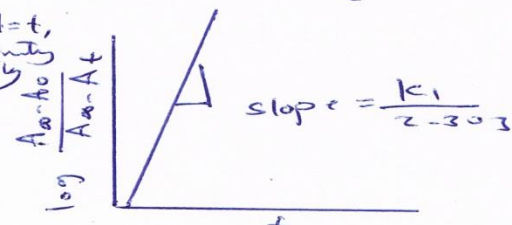
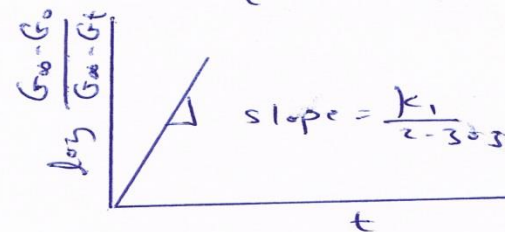
$$k_1 = \frac{2.303}{t} \log \frac{G_\infty - G_0}{G_\infty - G_t}$$

G_0, G_t & G_∞ electric conductivity at $t=0, t=t,$

→ By using the absorption

$$k_1 = \frac{2.303}{t} \log \frac{A_\infty - A_0}{A_\infty - A_t}$$

A_0, A_t & A_∞ Absorption at $t=0, t=t$ & t infinity respectively

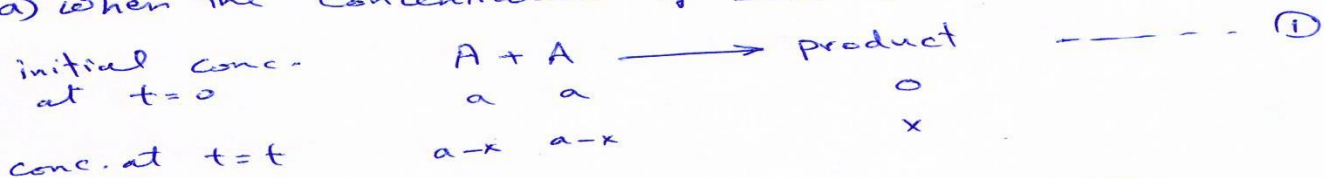


(12)

Second Order Reaction:

"When the sum of the powers of concentration term in the experimentally established rate equation is two, it is said to be a second order reaction",

a) when the concentration of both reactants is same:



$$\therefore \frac{dx}{dt} \propto (a-x)^2 \quad \text{----- (2)}$$

$$\therefore \frac{dx}{dt} = k_2 (a-x)^2 \quad \text{----- (3)}$$

where: k_2 is rate constant for second order reaction.

$$\therefore \int_0^x \frac{dx}{(a-x)^2} = k_2 \int_0^t dt \quad \text{----- (4)}$$

$$\therefore \int_0^x (a-x)^{-1} dx = k_2 \int_0^t dt \quad \text{----- (5)}$$

$$\frac{(a-x)^{-1}}{-1} \cdot x(-1) = k_2 t + C \quad \text{----- (6)}$$

$$\frac{1}{a-x} = k_2 t + C \quad \text{----- (7)}$$

when $t=0$ and $x=0$

$$\therefore \frac{1}{a} = C \quad \text{----- (8)}$$

substituted in eq. (7)

$$\therefore \frac{1}{a-x} = k_2 t + \frac{1}{a} \quad \text{----- (9)}$$

(13)

$$\therefore k_2 t = \frac{1}{a-x} - \frac{1}{a} \quad \text{----- (10)}$$

$$\therefore k_2 t = \frac{a - (a-x)}{a(a-x)} \quad \text{----- (11)}$$

$$\therefore k_2 t = \frac{\cancel{a} - \cancel{a} + x}{a(a-x)} \quad \text{----- (12)}$$

$$\therefore k_2 t = \frac{x}{a(a-x)} \quad \text{----- (13)}$$

$$\therefore \boxed{k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)}} \quad \text{----- (14)}$$

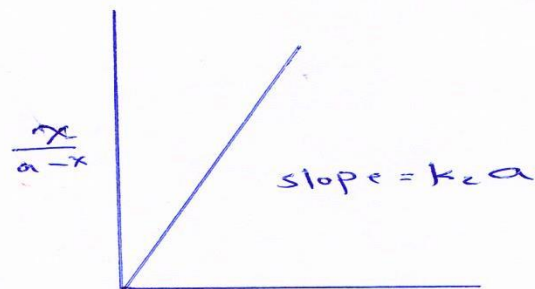
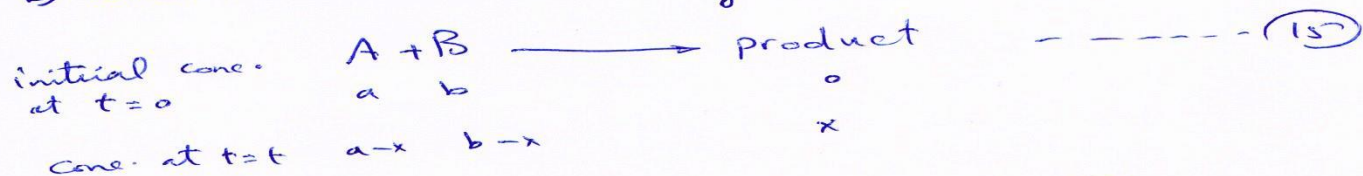


Fig (c) : The relation of $\frac{x}{a-x}$ vs t

b) When the concentrations of both reactants are different



$$\frac{dx}{dt} \propto (a-x)(b-x) \quad \text{----- (16)}$$

$$\frac{dx}{dt} = k_2 (a-x)(b-x) \quad \text{----- (17)}$$

$$\therefore \int_0^x \frac{dx}{(a-x)(b-x)} = k_2 \int_0^t dt \quad \text{----- (18)}$$

$$\therefore \frac{1}{a-b} \int_0^x \left[\frac{(a-x) - (b-x)}{(a-x)(b-x)} \right] dx = k_2 \int_0^t dt \quad \text{----- (19)}$$

$$\therefore \frac{1}{a-b} \int_0^x \left[\frac{\cancel{(a-x)}}{\cancel{(a-x)}(b-x)} - \frac{\cancel{(b-x)}}{(a-x)\cancel{(b-x)}} \right] dx = k_2 \int_0^t dt \quad \text{--- (20)}$$

$$(14) \quad \therefore \frac{1}{a-b} \int_0^x \left[\frac{dx}{(b-x)} - \int_0^x \frac{dx}{(a-x)} \right] = k_2 \int_0^t dt \quad \text{----- (21)}$$

$$\therefore \frac{1}{a-b} [-\ln(b-x) + \ln(a-x)] = k_2 t + C \quad \text{----- (22)}$$

$$\therefore \frac{1}{a-b} \left[\ln \frac{(a-x)}{(b-x)} \right] = k_2 t + C \quad \text{----- (23)}$$

when $t=0$, $x=0$

$$\therefore \frac{1}{a-b} \left[\ln \frac{a}{b} \right] = 0 + C \quad \text{----- (24)}$$

Substituting value of C in eq (23)

$$\therefore \frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} \right] = k_2 t + \frac{1}{(a-b)} \ln \frac{a}{b} \quad \text{----- (25)}$$

$$\therefore k_2 t = \frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} \right] - \frac{1}{(a-b)} \ln \frac{a}{b} \quad \text{----- (26)}$$

$$\therefore k_2 t = \frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} \right] - \ln \frac{a}{b} \quad \text{----- (27)}$$

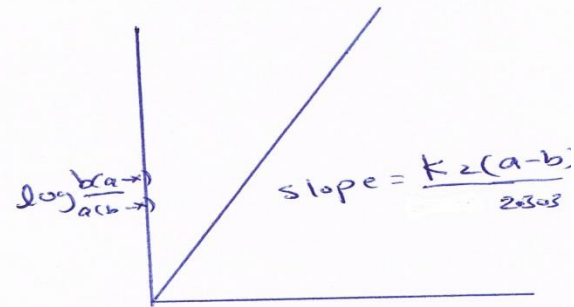
$$\therefore k_2 t = \frac{1}{(a-b)} \ln \left(\frac{(a-x)}{(b-x)} \times \frac{b}{a} \right) \quad \text{----- (28)}$$

$$\therefore \boxed{k_2 t = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}} \quad \text{----- (29)}$$

$$\therefore \boxed{k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}} \quad \text{----- (30)}$$

Unit of Second order reaction

$$\text{Unit} = (\text{Conc})^{1-n} \cdot \text{Time}^{-1} \quad \text{----- (31)}$$



Fig(1) relationship for $\log \frac{b(a-x)}{a(b-x)}$ vs t

(15)

$$= (\text{Conc.})^{1-2} \cdot \text{Time}^{-1} \quad \text{--- (32)}$$

$$\boxed{\text{Unit} = \text{mol}^{-1} \text{L s}^{-1}} \quad \text{--- (33)}$$

$$\text{or } k_2 = \frac{1}{at} \cdot \frac{x}{a-x} \quad \text{--- (34)}$$

$$k_2 = \frac{1}{\text{Conc.} \cdot \text{Time}} = (\text{Conc.} \cdot \text{Time})^{-1} \quad \text{--- (35)}$$

$$\boxed{k_2 \text{ Unit} = \text{mol}^{-1} \text{L s}^{-1}} \quad \text{--- (36)}$$

Half time period :

$$\therefore k_2 = \frac{1}{at} \cdot \frac{x}{a-x} \quad \text{--- (37)}$$

$$\text{at } t = t_{1/2} \quad \text{and} \quad x = \frac{1}{2}a$$

$$\therefore k_2 = \frac{1}{a \cdot t_{1/2}} \cdot \frac{a/2}{(a - a/2)} \quad \text{--- (38)}$$

$$\therefore k_2 = \frac{1}{a \cdot t_{1/2}} \cdot \frac{a/2}{a/2} \quad \text{--- (39)}$$

$$\therefore \boxed{t_{1/2} = \frac{1}{k_2 a}} \quad \text{--- (40)}$$

$$\left\{ \begin{aligned} a - \frac{a}{2} &= \frac{2a - a}{2} \\ &= \frac{a}{2} \end{aligned} \right.$$



$$\frac{dx}{dt} = k_2 [\text{CH}_3\text{COO C}_2\text{H}_5]^1 [\text{OH}^-]^1 \quad \text{--- (42)}$$

$$\therefore \text{Order} = 1 + 1 = 2$$

(15)

* When one of the reactant is present in excess.

Let $a \gg b$

Then $a-b \approx a$, $a-x \approx a$

$$\therefore K_2 = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)} \quad \text{----- (43)}$$

$$\therefore K_2 = \frac{2.303}{a-t} \log \frac{b \times a}{a(b-x)} \quad \text{----- (44)}$$

$$\therefore K_2 a = \frac{2.303}{t} \log \frac{b}{b-x} \quad \text{----- (45)}$$

Assumption $\boxed{K_2 a = k_1}$ ----- (46)

$$\therefore \boxed{k_1 = \frac{2.303}{t} \log \frac{b}{b-x}} \quad \text{----- (47)}$$

So, when one of the reactant is present in excess, a secondary order reaction reduces to a first order reaction.

Third Order Reaction:

"when the sum of the power of concentration term in the experimentally established rate equation is three, then it is known as third order reaction."

when the conc. of all the reactants is same ----- (1)



initial conc.
at $t=0$

$a \quad a \quad a$
 $a-x \quad a-x \quad a-x$

0
 x

conc. at $t=t$

$$\frac{dx}{dt} \propto (a-x)^3 \quad \text{----- (2)}$$

$$(17) \therefore \frac{dx}{dt} = k_3 (a-x)^3 \quad \text{--- (3)}$$

$$\therefore \int_0^x \frac{dx}{(a-x)^3} = k_3 \int_0^t dt \quad \text{--- (4)}$$

$$\therefore \int_0^x (a-x)^{-3} dx = k_3 \int_0^t dt \quad \text{--- (5)}$$

$$\therefore \frac{(a-x)^{-3+1}}{-2} \times (-1) = k_3 t + C \quad \text{--- (6)}$$

or

$$\frac{1}{2(a-x)^2} = k_3 t + C \quad \text{--- (7)}$$

When $t=0$ and $x=0$

$$\frac{1}{2(a-0)^2} = k_3 \times 0 + C \quad \text{--- (8)}$$

$$\therefore \frac{1}{2a^2} = C \quad \text{--- (9)}$$

substitution in eq. (8)

$$\therefore \frac{1}{2(a-x)^2} = k_3 t + \frac{1}{2a^2} \quad \text{--- (10)}$$

$$\therefore k_3 t = \frac{1}{2(a-x)^2} - \frac{1}{2a^2} \quad \text{--- (11)}$$

Unit of Third Order Reaction

$$\therefore k_3 = \frac{1}{2t(a-x)^2} - \frac{1}{2a^2} \quad \text{--- (12)}$$

$$\therefore = \frac{1}{\text{Time (conc)}^2} \quad \text{--- (13)}$$

$$\boxed{\text{Unit of } k_3 = (\text{mol} \cdot \text{L})^{-2} \text{ Time}^{-1}} \quad \text{--- (14)}$$

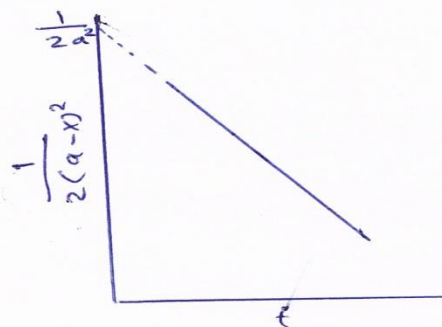


Fig () : Relationship between $\frac{1}{2(a-x)^2}$ and t for 3rd order reaction

$$\begin{aligned} \text{Unit} &= (\text{Conc.})^{1-n} \cdot \text{Time}^{-1} \quad \text{--- (15)} \\ &= (\text{Conc.})^{1-3} \cdot \text{Time}^{-1} \quad \text{--- (16)} \\ \text{Unit of } k_3 &= (\text{Conc.})^{-2} (\text{Time})^{-1} \quad \text{--- (17)} \end{aligned}$$

Half time period

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

$$k_3 t = \frac{1}{2(a-x)^2} - \frac{1}{2a^2} \quad \text{--- (18)}$$

$$k_3 t_{1/2} = \frac{1}{2(a - \frac{a}{2})^2} - \frac{1}{2a^2} \quad \text{--- (19)}$$

$$k_3 t_{1/2} = \frac{1}{2(\frac{2a-a}{2})^2} - \frac{1}{2a^2} \quad \text{--- (20)}$$

$$k_3 t_{1/2} = \frac{\cancel{4}^2}{2a^2} - \frac{1}{2a^2} = \frac{4-1}{2a^2} = \frac{3}{2a^2} \quad \text{--- (21)}$$

$$\therefore t_{1/2} = \frac{3}{2a^2 \cdot k_3} \quad \text{--- (22)}$$

ex.



$$\frac{dx}{dt} = k_3 [\text{FeCl}_3]^2 [\text{SnCl}_2] \quad \text{--- (24)}$$

$$\therefore \text{Order} = 2 + 1 = 3$$

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Determination of the order of a reaction:

There are a number of methods to determine the order of reaction:

① Differential Method (Vant Hoff's Differential Method):

The rate of an n order reaction equal

$$-\frac{dC}{dt} = R = k C^n \quad \text{----- ①} \quad R = \text{reactant}$$

For two experiments having initial concentration C_1 and C_2 , therefore:

$$-\frac{dC_1}{dt} = R_1 = k C_1^n \quad \text{----- ②}$$

$$-\frac{dC_2}{dt} = R_2 = k C_2^n \quad \text{----- ③}$$

On dividing

$$\therefore \frac{-\frac{dC_2}{dt}}{-\frac{dC_1}{dt}} = \left(\frac{C_2}{C_1}\right)^n \quad \text{----- ④}$$

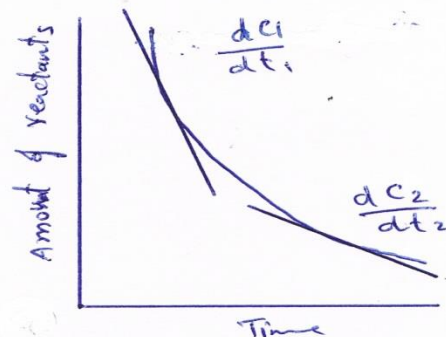


Fig 1 : Relation between amount of reactants & Time

$$\log \left(\frac{-dC_2}{dt} \right) - \log \left(\frac{-dC_1}{dt} \right) = n (\log C_2 - \log C_1) \quad \text{----- ⑤}$$

$$\therefore n = \frac{\log \left(\frac{-dC_2}{dt} \right) - \log \left(\frac{-dC_1}{dt} \right)}{\log C_2 - \log C_1} \quad \text{----- ⑥}$$

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② Integration Method (Hit and Trial Method)

By substituted the value of a or x and other values in integrate equation for rate constant.

$$k_0 = \frac{x}{t} \quad \text{----- 0th order (7)}$$

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{----- 1st order (8)}$$

$$k_2 = \frac{1}{at} \cdot \frac{x}{(a-x)} \quad \text{----- 2nd order (9) (Same Conc.)}$$

$$k_2 = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)} \quad \text{----- 2nd order (10) (different conc.)}$$

If the values of k_0 are fixed or similar, the order = 0 but, if not, must trial by using eq-s (8) or (9) or (10) and the values of k_1 are fixed or similar that produce the value of order = 1.

Disadvantage of this method is required long time for calculations.

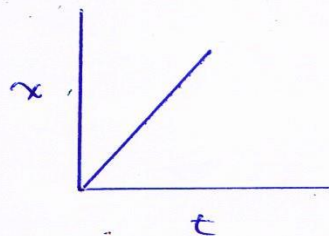
③ Graphic Method

By drawing the graphic between remaining of conc. and time.

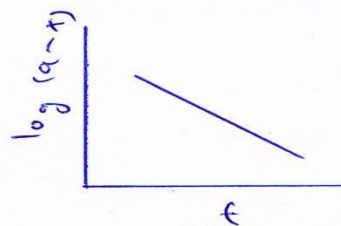
If the graph give a linear relationship in the certain order that good, but if the relationship isn't linear, therefore, we must use the other graph.

(21)

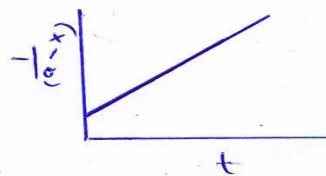
According to the figures () a, b, c, d



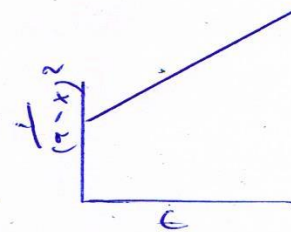
a) Zero order



b) First order



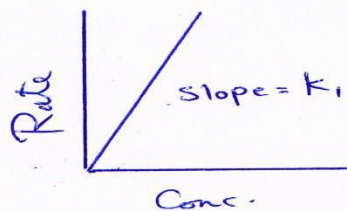
c) Second order



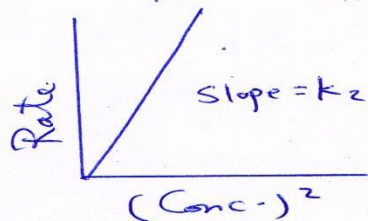
d) Third order

Fig () : Graphic Method for Zero, first, Second & third orders

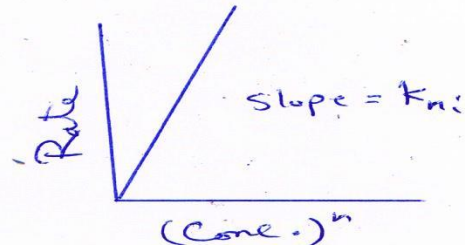
Or by drawing the rate vs $(\text{Conc.})^n$, $n = 1, 2 \dots n_i$ according to fig () a, b & c.



a) first order



b) Second order



c) n_i Order

Fig () : Graphic Method by drawing Rate vs $(\text{Conc.})^n$
So, $n = 1, 2 \dots n_i$

* Disadvantage of this method is required long time for calculations.

(22)

(4) Half Time Method :

This method is very important and very simple in applications, it related with initial concentration by

$$t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{--- (11)}$$

$$\text{So, } t_{1/2} \propto \frac{1}{a_1^{n-1}} \quad \& \quad t_{1/2} \propto \frac{1}{a_2^{n-1}} \quad \text{--- (12)}$$

on dividing :

$$\boxed{\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}} \quad \text{--- (13)}$$

Taking log both sides

$$\log(t_{1/2})_1 - \log(t_{1/2})_2 = (n-1)[\log a_2 - \log a_1] \quad \text{--- (14)}$$

$$(n-1) = \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1} \quad \text{--- (15)}$$

$$\&\& \boxed{n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}} \quad \text{--- (16)}$$

$$\underline{\text{or}} \quad \therefore t_{1/2} \propto \frac{1}{a_0^{n-1}} \quad \text{--- (17)}$$

$$\therefore t_{1/2} = C (a_0)^{n-1} \quad \text{--- (18)}$$

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Taking log for both sides

$$\therefore \log t_{1/2} = (1-n) \log a_0 + \log C \quad \text{--- (19)}$$

or

From eq. (13), by taking log for both sides

$$\therefore \log \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \log \frac{a_2}{a_1} \quad \text{--- (20)}$$

eq. (20) may draw by fig ()

a_1, a_2 & $\frac{a_1}{2}, \frac{a_2}{2}$ were determined on curve to find $(t_{1/2})_1$ and $(t_{1/2})_2$

and substituted in eq. (20) to calculate n (order of reaction)

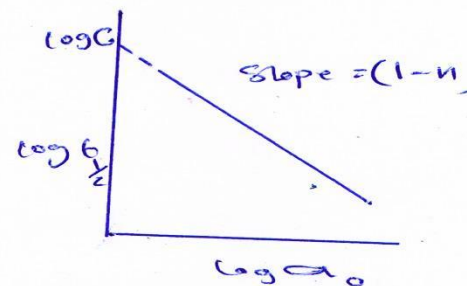


Fig 1: The relation of $\log t_{1/2}$ vs $\log a_0$

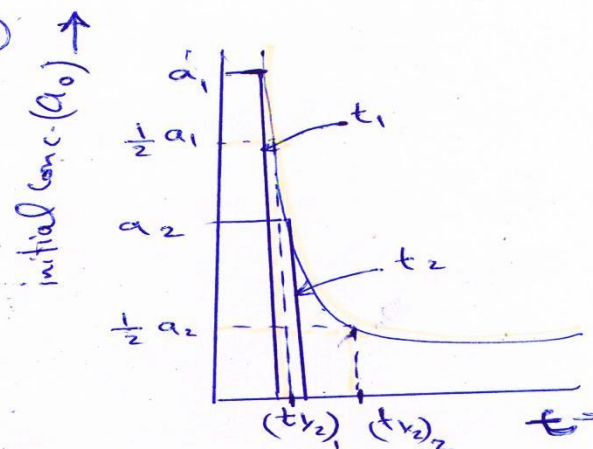


Fig 2: Relation between initial conc. & time.

5) Ostwald's isolated Method

If all reactants in a reaction except one are present in very large, the order is determined by depending on other, this method used for the complex reaction especially.

$$\frac{dx}{dt} = k (a-x)^{n_1} (b-x)^{n_2} \quad \text{--- (21)}$$

(24)

if (b) has a very large conc., thereby:

$$\bar{k} = k (b-x)^{n_2} \quad \text{--- (22)}$$

$$\therefore \frac{dx}{dt} = \bar{k} (a-x)^{n_1} \quad \text{--- (23)}$$

\therefore order of reaction = n_1

& if (a) only has a very large conc., thereby:

$$\bar{k} = k (a-x)^{n_1} \quad \text{--- (24)}$$

$$\therefore \frac{dx}{dt} = \bar{k} (b-x)^{n_2} \quad \text{--- (25)}$$

So, order of reaction = n_2

The Total Order of reaction = $n_1 + n_2$ --- (26)

So, This method used for reaction having more than reactant, and considered this reaction is Pseudo reaction by fixing the conc. of one or more substances, therefore, the concentration of these substances not affected after the reaction is completed.



**THANK YOU
FOR YOUR
ATTENTION**