D. B. College (Jaynagar) Lect – 19

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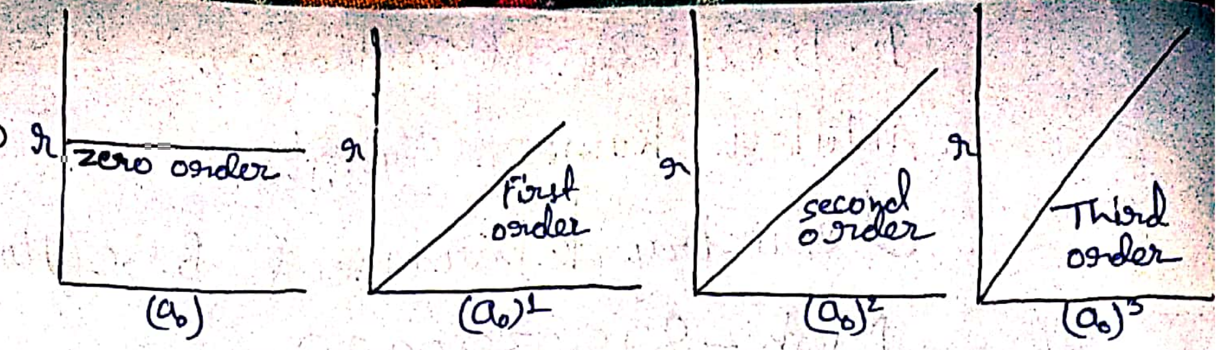
1. Expression for rate constants for reactions of different orders.

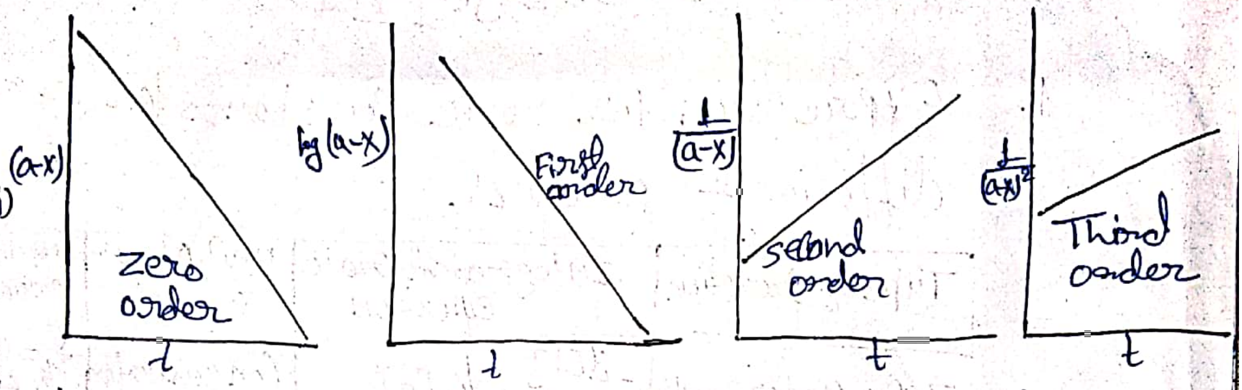
Type of reaction	Integrated rate equation	Unit of rate constant	Half life period	3/4 life Period
zero order reaction	$-\frac{d[A]}{dt} = k_0[A]^0$ Differentiation from $\frac{dx}{dt} = k$	Concentration time^{-1}	$t_{\frac{1}{2}} = \frac{a}{2k_0}$	—
First order reaction	$K_1 = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$	time^{-1}	$t_{\frac{1}{2}} = \frac{0.693}{K_1}$	$t_{\frac{3}{4}} = 2\frac{0.693}{k_1} - \frac{1.382}{k_1}$
Second order reaction	$K_2 = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$ Diffential form $\frac{dx}{dt} = k(a-x)^2$	mole^{-1} litre time^{-1}	$t_{\frac{1}{2}} = \frac{1}{k_2 a}$	$t_{\frac{3}{4}} = \frac{3}{k_2 a}$
Third order reaction	$K_3 = \frac{x(2a-x)}{t 2a^2(a-x)^2}$ Differential form $\frac{dx}{dt} = k(a-x)^3$	litre^2 mole^{-2} time^{-1}	$t_{\frac{1}{2}} = \frac{3}{2k_3 a^2}$	—

2. Some typical linear plots for reactions of different orders:

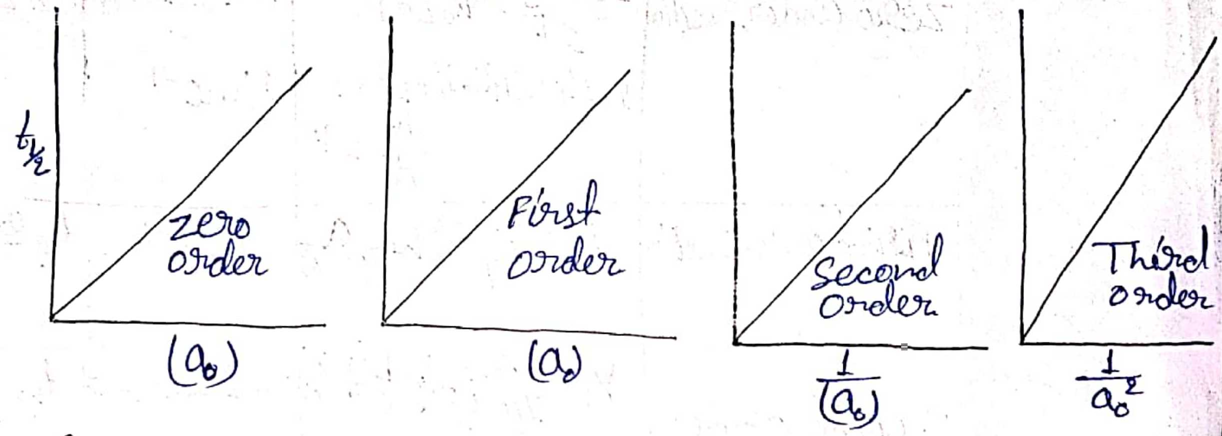
(i)



(ii)



(iii)



3. Amount left after n half-lives $= \left(\frac{1}{2}\right)^n [A]_0$

No. of half-lines $= \frac{\text{Total time}}{t_{1/2}}$

4. Exponential form of expression for rate constant for reaction of 1st order: $[A] = [A]_0 e^{-kt}$
or $C_t = C_0 e^{-kt}$

5. $t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$

t respectively.

6. Arrhenius equation for effect of temperature on rate constant,

$$k = Ae^{-E_a/RT}$$

on $\log k = \log R - \frac{E_a}{2.303RT}$

Also, $\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$

If k_1 and k_2 are rate constants at temperature T_1 and T_2, then

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

7. Example of reactions of 1st order and their formula for rate constants

(i) $2N_2O_5 \longrightarrow 4NO_2 + O_2$; $k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$

where V_∞ and V_t are volumes of N_2 gas collected after infinity time and after time t respectively.

(ii) $H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$; $k = \frac{2.303}{t} \log \frac{V_0}{V_t}$

where V_0 and V_t are the volumes of $KMnO_4$ solution used for titrating a definite volume of the reaction mixture at $t = 0$ and at time t respectively.

(ii) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

(iii) $NH_4NO_2 \longrightarrow 2H_2O + N_2$; $K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$

where V_∞ and V_t are volumes of N_2 gas collected after infinity time and after time t respectively.

(iv) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

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

Where V_0, V_t and V_∞ are the volume of NaOH solution used for titration mixture at zero time, after time t and after infinity respectively.

(V) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Glucose Fructose

$$K = \frac{2.303}{t} \log \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$$

where r_0, r_t and r_∞ are the polarimetric reading at zero time t and after infinity respectively.