D. B. College (Jaynagar) Lect-5
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Half-life of a n^{th} order reaction

Let us find out $t_{1/2}$ for n^{th} order reaction where $n \neq 1$.

$$\therefore \frac{-d[A]}{dt} = K_n[A]^n \Rightarrow \frac{-d[A]}{[A]^n} = Kdt \Rightarrow \int_{[A]_0}^{[A]_{0/2}} \frac{d[A]}{[A]^n} = K\int_0^{t_{1/2}} dt$$

$$\int_{[A]_{0/2}}^{[A]_0} [A]^{-n} d[A] = K_n t_{1/2} \qquad \left[\frac{[A]^{1-n}}{1-n}\right]_{[A]_{0/2}}^{[A]_0} = K_n t_{1/2}$$

$$\Rightarrow \frac{1}{1-n}\left([A]_0^{1-n} - \left[\frac{[A]_0}{2}\right]^{1-n}\right) = K_n t_{1/2} = \frac{[A]_0^{1-n}}{1-n}\left[1-\left(\frac{1}{2}\right)^{1-n}\right] = K_n t_{1/2}$$

$$\Rightarrow \frac{1}{(1-n)[A]_0^{1-n}}\left[1-2^{n-1}\right] = K_n t_{1/2} \Rightarrow \frac{2^{n-1}-1}{K_n(n-1)[A]_0} = t_{1/2} \text{ (order } n \neq 1)$$

Therfore for n^{th} order reaction, the half-life is inversely related to the initial Concentration raised to the power of $(n-1)$.

$t_{1/2} \propto \frac{1}{a^{n-1}}$

where n = order of reaction.

Example: (i) All radioactive reactions

(ii) A ⟶ Product

(iii) $2NO \rightleftharpoons 2N_2 + O_2$

(iv) $2Cl_2O_7 \longrightarrow 2Cl_2 + 7O_2$

(A) Unit of rate constant of first order reaction

$K = (sec)^{-1}$ $\Delta n = 1$

(B) Velocity constant for first order reaction

$$K_1 = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \Rightarrow t = \frac{2.303}{K_1} \log_{10} \frac{a}{(a-x)}$$

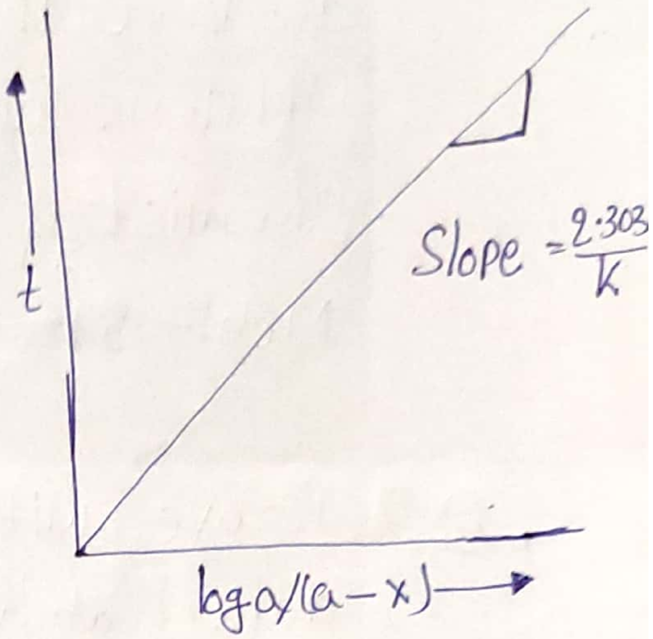
where t = time, a = initial concentration at t=0

(a−x) = concentration after time t

K = Rate constant

(C) Graphical Representation

Graph between t v/s $\log \frac{a}{(a-x)}$ is a straight line



EX. 21 A first order reaction gets 90% completed in 40 minutes. Find out the half-life period of the reaction.

Sol. Suppose that the initial concentration of reactant

$(a) = 100 \qquad t = 40$ minutes

Therefore,

$$x = 90$$

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

$$= \frac{2.303}{40} \log \frac{100}{100-90} \Rightarrow k_1 = \frac{2.303}{40} \log 10$$

$$= \frac{2.303}{40} \, 1 = 5.757 \quad 10^{-2} \text{ minutes}^{-1}$$

$$t_{1/2} = \frac{0.693}{5.757 \; 10^{-2}} = 10.3 \text{ minutes}^{-1}$$