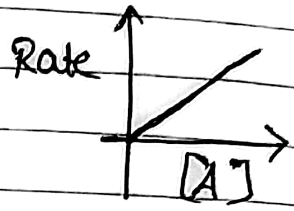
Chemical Kinetics – 06

First Order Kinetics

$$A \longrightarrow B$$



Rate of Reaction $= r = K[A]^1$

Rate decreases as conc of reactant decreases.

Integrated Rate Law.

$$A \longrightarrow B$$

$$rate = r = K[A]^1$$

$$\& \ rate = r = \frac{-1}{1}\frac{dA}{dt}$$

$\Rightarrow$

$$\frac{-1}{1}\frac{dA}{dt} = K[A]^1$$

$$\int_{A_0}^{A} \frac{dA}{A} = \int_0^t -K\,dt$$

Let
at $t = 0$ $A = A_0$
at $t = t$ $A = A$

$$[\log_e A]_{A_0}^{A} = -K(t)_0^t$$

$$\log_e A - \log_e A_0 = -Kt$$

$$\boxed{\log_e A = \log_e A_0 - Kt}$$ Integrated Rate Law for Ist order

Note: $\log_e x = 2.303 \log_{10} x$

$\Rightarrow$

$$2.303 \log_{10} A = 2.303 \log_{10} A_0 - Kt$$

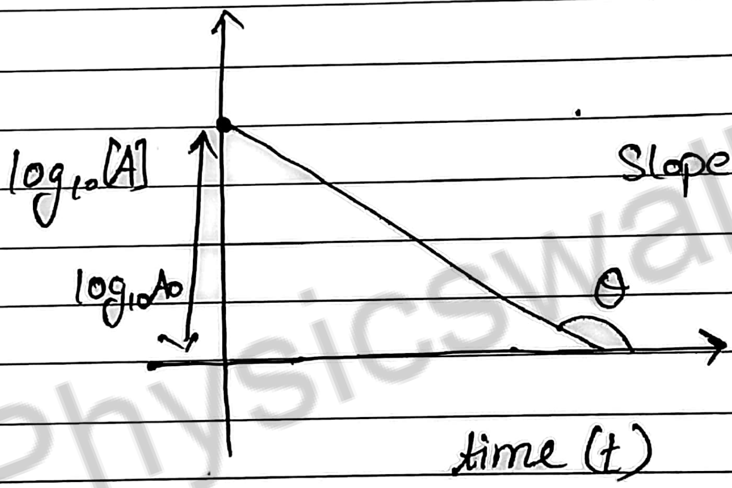
$$\boxed{\log_{10} A = \log_{10} A_0 - \frac{Kt}{2.303}}$$ Integrated Rate Law

First order Kinetics

Graph of $\log_{10} A$ v/s t

$$\log_{10} A = \frac{-Kt}{2.303} + \log_{10} A_0$$

$$y = mx + c$$



$$\text{Slope} = \tan\theta = -\frac{K}{2.303}$$

The plot of log of Conc v/s time is a straight line for First order reaction.

Other forms of this rate Law :-

① $\Rightarrow$ for numericals

$$\log_{10} A = \log_{10} A_0 - \frac{Kt}{2.303}$$

$$\log_{10} A_0 - \log_{10} A = \frac{Kt}{2.303}$$

$$\log_{10} \frac{A_0}{A} = \frac{Kt}{2.303}$$

Learn & Use this Always

$$\boxed{K = \frac{2.303}{t} \log_{10} \frac{A_0}{A}}$$

$A_0 \rightarrow$ initial conc

$A \rightarrow$ remaing conc

② exponential form. (Don't use unless specifically asked)

$$\log_e A = \log_e A_0 - kt$$

$$kt = \log_e A_0 - \log_e A$$

$$kt = \log_e\left(\frac{A_0}{A}\right)$$

$$\frac{A_0}{A} = e^{kt}$$

$$\frac{A}{A_0} = e^{-kt}$$

$$\boxed{A = A_0 e^{-kt}}$$

A → Remaing Conc

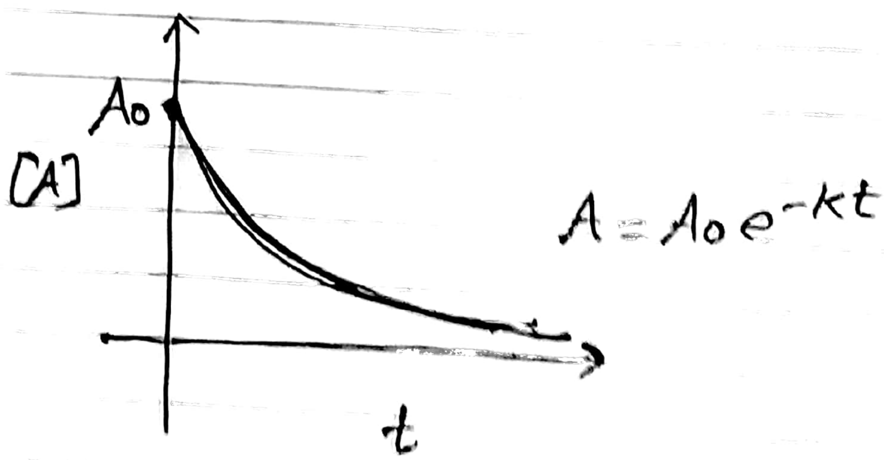
A_0 → initial Conc.

Graph of conc of reactant [A] v/s time 't'

$A = A_0 e^{-kt}$

$t \to 0$
$A \to A_0$

$t \to \infty$
$A \to 0$



* $\log_{10} 2 = 0.3$ $\log_{10} 5 = 0.7$
$\log_{10} 3 = 0.48$ $\log_{10} 7 = 0.85$

Learn these values → will be used in Ist order

Half Life of Reaction

at $t = t_{1/2}$

$A = \frac{A_0}{2}$

$$K = \frac{2.303}{t} \log_{10} \frac{A_0}{A}$$ ← use this form always

$$K = \frac{2.303}{t_{1/2}} \log_{10} \frac{A_0}{\frac{A_0}{2}}$$

$$t_{1/2} = \frac{2.303}{K} \log_{10} 2^{*}$$

$$t_{1/2} = \frac{2.303 \times 0.3}{K}$$

$$\boxed{t_{1/2} = \frac{0.693}{K}}$$ remember

Half Life First order
↓
do not depend On initial concentration A_0

{ zero order $t_{1/2} = \frac{A_0}{2K}$ }

Life time of Reaction

at $t = t_{lf}$

$A = 0$

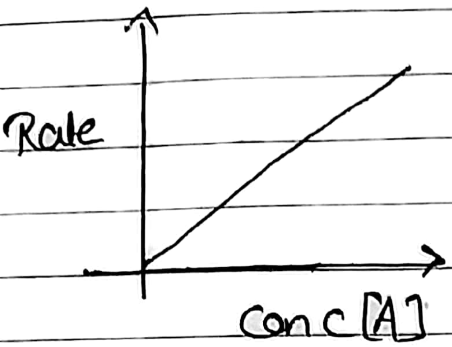
$$K = \frac{2.303}{\cancel{t}} \log_{10} \frac{A_0}{A}$$

$$t_{lf} = \frac{2.303}{K} \log_{10} \frac{A_0}{0}$$

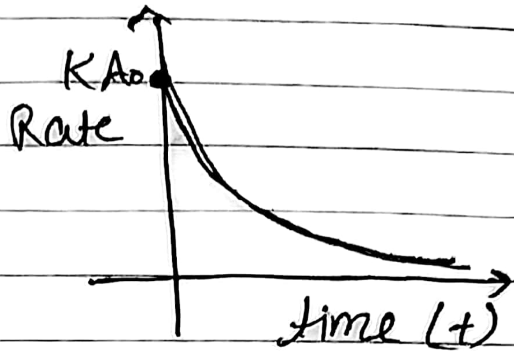
$t_{lf} \rightarrow \infty$ never completes theoretically

First order reaction never completes 100%.

Graphs of First Order Kinetics



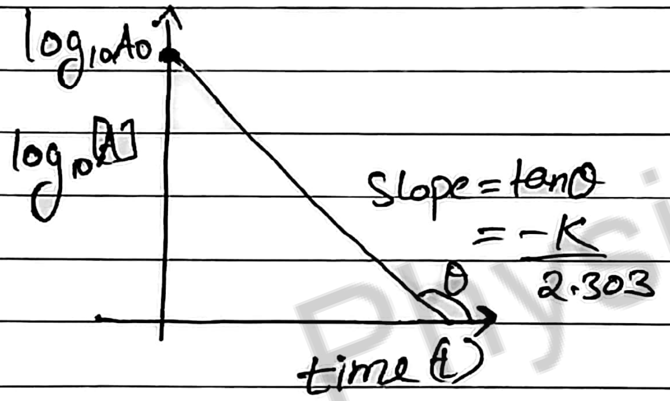
$$r = K[A]^1$$



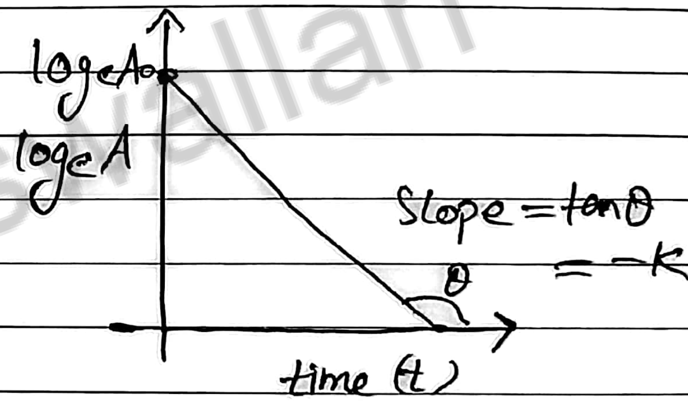
$$r = K[A]^1 = KA_0 e^{-Kt}$$

$t \to 0 \quad r \to KA_0$

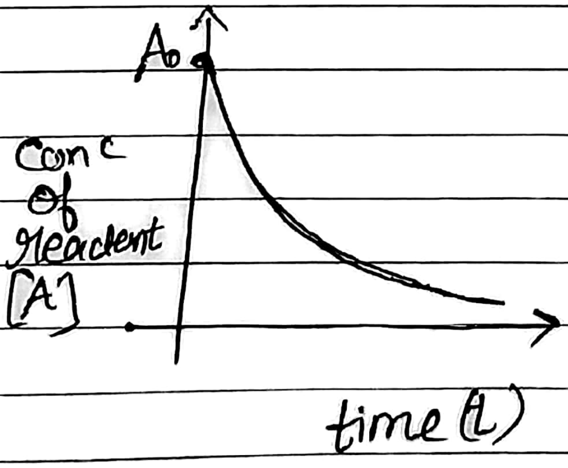
$t \to \infty \quad r \to 0$



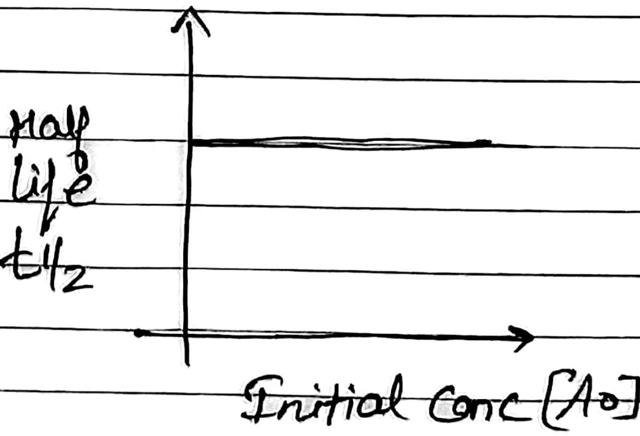
$$\log_{10} A = \log_{10} A_0 - \frac{Kt}{2.303}$$



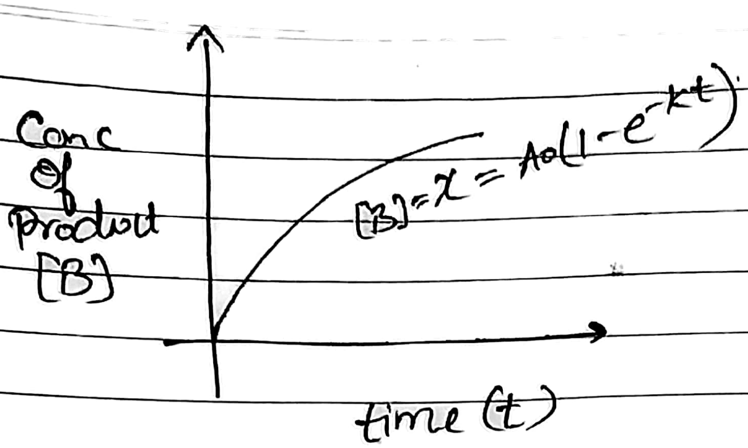
$$\log_e A = \log_e A_0 - Kt$$



$$A = A_0 e^{-Kt}$$



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



$$A \longrightarrow B$$

$t=0 \quad A_0 \qquad -$

$t=t \quad A_0 - x \qquad x$

$$A = A_0 e^{-kt}$$

$$(A_0 - x) = A_0 e^{-kt}$$

$$x = A_0 - A_0 e^{-kt}$$

$$x = A_0(1 - e^{-kt})$$

$t \to 0 \qquad\qquad t \to \infty$

$x \to 0 \qquad\qquad x \to A_0$

<u>Some Questions</u>

use $K = \dfrac{2.303}{t} \log_{10} \dfrac{A_0}{A}$ ($A_0 \rightarrow$ initial conc, $A \rightarrow$ remaing conc)

<u>Q1)</u> A first order reaction is 20% complete in 5 min. Calculate the time taken to complete 60% of the reaction.

<u>Solution</u>

$$t = \frac{2.303}{K} \log_{10} \frac{A_0}{A}$$

20% completion

$A_0 = 100$

$A = 80$

$t = 5\,min$

$$5\,min = \frac{2.303}{K} \log_{10} \frac{100}{80} \quad \text{(i)}$$

60% completion

$A_0 = 100$ $\quad t = \frac{2.303}{K} \log_{10} \frac{100}{40}$ (ii)

$A = 40$

$t = ?$

(ii) ÷ (i)

$$\frac{t}{5} = \frac{\log_{10} \frac{10\cancel{0}}{4\cancel{0}}}{\log_{10} \frac{10\cancel{0}}{8\cancel{0}}}$$

$$\frac{t}{5} = \frac{\log_{10} 10 - \log_{10} 4}{\log_{10} 10 - \log_{10} 8} = \frac{1 - 2\log_{10} 2}{1 - 3\log_{10} 2} = \frac{1 - 2\times 0.3}{1 - 3\times 0.3}$$

$$\frac{t}{5} = \frac{0.4}{0.1} \Rightarrow \boxed{t = 20 \text{mins}}$$

Q2) In a first order reaction the concentration of reactant decreases from 800 mol/dm³ to 50 mol/dm³ in 2×10^4 s. The rate constant of reaction is :-

a) 2×10^4 b) 3.4×10^{-4} c) 1.38×10^{-4} d) 2×10^{-4}

Solution

$$K = \frac{2.303}{t} \log_{10} \frac{A_0}{A}$$

$$= \frac{2.303}{2\times10^4} \log_{10} \frac{80\cancel{0}}{5\cancel{0}}$$

$$= \frac{2.303}{2\times10^4} \times 4\log_{10} 2 = \frac{2.303\times4\times0.3}{2\times10^4}$$

$$\simeq 1.38\times10^{-4}$$

Q3) $A \longrightarrow$ Product is first order

Conc of A changes from 0.1M to 0.025M in 40 min. Find the rate of Reaction of A when concentration of A is 0.01M

a) $3.47 \times 10^{-4}\ M\,min^{-1}$ c) $1.73 \times 10^{-4}\ M\,min^{-1}$

b) $3.47 \times 10^{-5}\ M\,min^{-1}$ d) $1.73 \times 10^{-5}\ M\,min^{-1}$

Solution

$$K = \frac{2.303}{t} \log_{10} \frac{A_0}{A}$$

$$= \frac{2.303}{40} \log_{10} \frac{0.100}{0.025}$$

$$= \frac{2.303}{40} 2 \log_{10} 2$$

$$= \frac{2.303}{40} \times 2 \times 0.3 = \frac{13.818}{400} = 3.454 \times 10^{-2}$$

$$Rate = K[A]^1$$

$$= 3.45 \times 10^{-2} \times 0.01$$

$$= 3.45 \times 10^{-4} \simeq 3.47 \times 10^{-4}\ M\,min^{-1}$$

Q4) $A \longrightarrow$ Product is first order

if $K = 6.93 \times 10^{-3} min^{-1}$

find i) $t_{1/2}$

ii) $t_{1/3}$

iii) $t_{2/3}$

Solution

i) $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{6.93 \times 10^{-3}} = 10^2 min = 100 min$

ii) $t_{1/3} = \frac{2.303}{K} \log_{10} \frac{A_0}{\frac{2}{3} A_0}$

$\downarrow$

$A_0 = A_0$

$A = \frac{2A_0}{3}$

$= \frac{2.303}{6.93 \times 10^{-3}} \log_{10} \frac{3}{2}$

$\frac{1}{3}$rd Complete Ho gaya

$\frac{2}{3}$ bacha

iii) $t_{2/3} = \frac{2.303}{K} \log_{10} \frac{A_0}{\frac{A_0}{3}}$

$\downarrow$

$A_0 = A_0$

$A = \frac{A_0}{3}$

$= \frac{2.303}{6.93 \times 10^{-3}} \log_{10} 3$

$t_{2/3} \rightarrow \frac{2}{3}$rd Complete ho gaya

$\frac{1}{3}$ Bacha

Shortcut $\boxed{t_f = \frac{2.303}{K} \log_{10} \frac{1}{1-f}}$

Two important Result

① $t_{75\%} = 2\,t_{50\%}$ → अगर कोई Reaction ये follow करे तो first order होगा

Proof:

$$t_{50\%} = \frac{2.303}{K}\log_{10}\frac{100}{50}$$

$$t_{75\%} = \frac{2.303}{K}\log_{10}\frac{100}{25}$$

$$\frac{t_{75\%}}{t_{50\%}} = \frac{\log_{10}4}{\log_{10}2} = 2$$

$$\boxed{t_{75\%} = 2\,t_{50\%}}$$

② $t_{99.9\%} = 10\,t_{1/2}$

Proof:

$$t_{50\%} = \frac{0.693}{K}$$

$$t_{99.9\%} = \frac{2.303}{K}\log_{10}\frac{100}{0.1}$$

$$= \frac{2.303}{K}\log_{10}10^3$$

$$t_{99.9\%} = \frac{2.303 \times 3}{K}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\frac{2.303 \times 3}{K}}{\frac{0.693}{K}}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{6.909}{0.693} \simeq 10$$

$$\boxed{t_{99.9\%} = 10\, t_{50\%}}$$

Similarly, After Calculations following results were obtained.

$t_{50\%} = t_{1/2}$

$t_{25\%} = 0.415 t_{1/2}$

$t_{75\%} = 2 t_{1/2}$

$t_{87.5\%} = 3 t_{1/2}$

$t_{99.9\%} = 10 t_{1/2}$

Examples of First Order Reaction → Remember these.

① Nuclear Physics → Radioactive Reaction
Radioactivity (decay)

② Growth or Decay of Bacteria

③ Inversion of Cane Sugar

$$\underset{\substack{\text{sucrose}\\(\text{dextro})}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{glucose}\\(\text{dextro})}}{C_6H_{12}O_6} + \underset{\substack{\text{fructose}\\(\text{leavo})\\(\text{more})}}{C_6H_{12}O_6}$$

④ Acidic Hydrolysis of Ester

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

⑤ Dissociation of N_2O_5

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

⑥ Dissociation of H_2O_2

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$