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S-I

(18) $t_{1/2} = 20\ min$

$Rate = k[A]$

$= \frac{\ln 2}{20} \times 0.2$

(19)

(20) $k = \frac{1}{1} \ln \frac{100}{98}$

$= \frac{1}{60} \ln \frac{100}{98}$

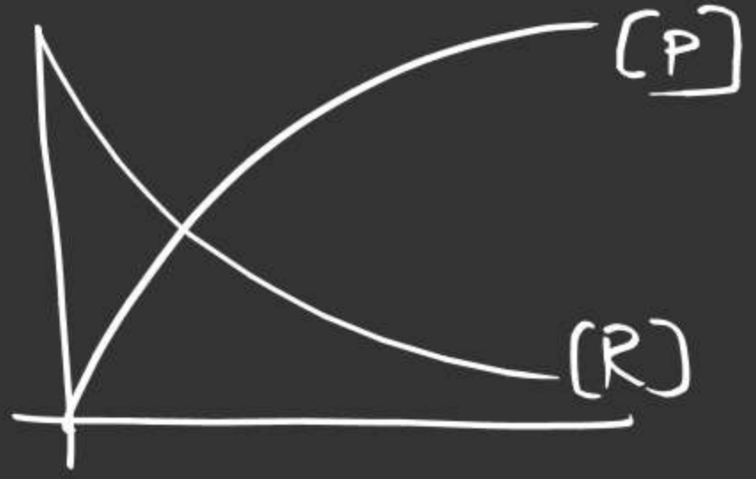
(20) $= 4 \times 10^{-3} \times 0.02$

$= 8 \times 10^{-5}$

(21) — D

(22) — B

(30)



(C)

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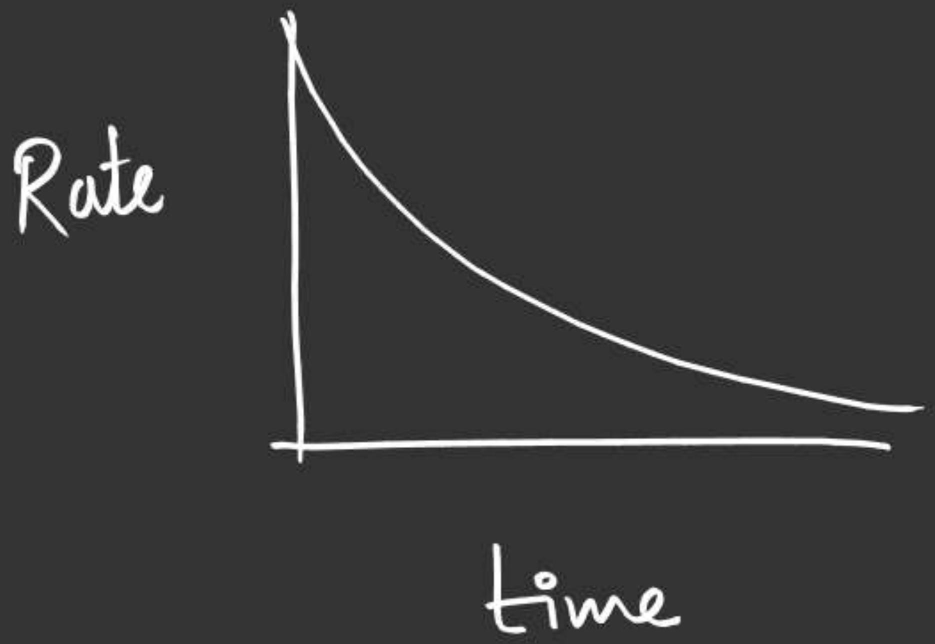
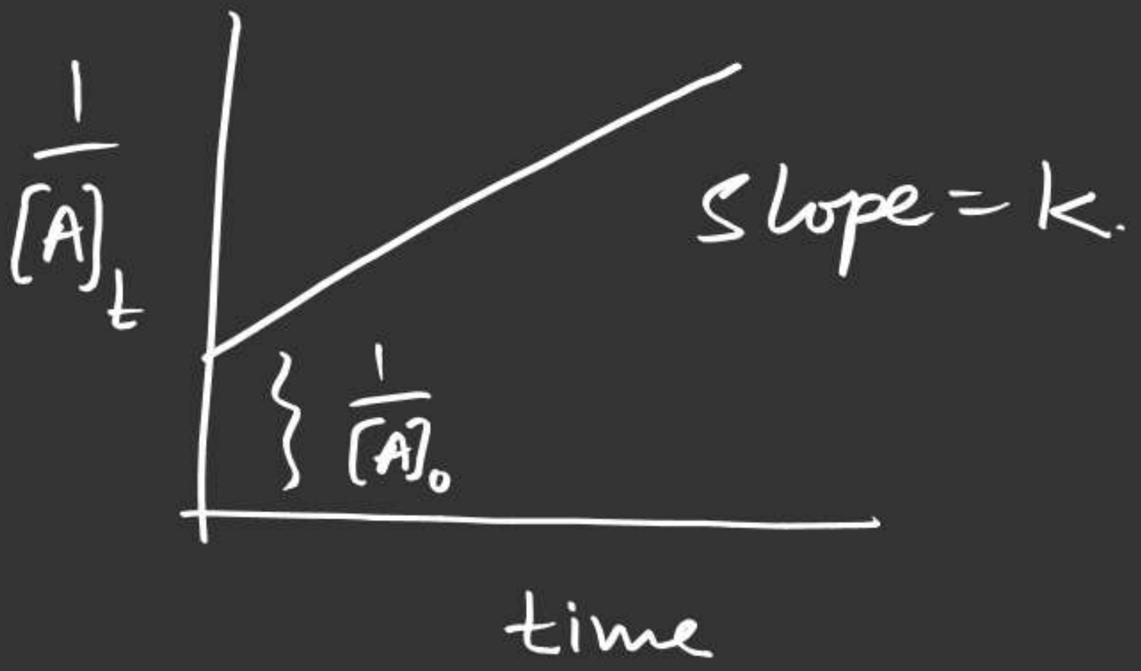
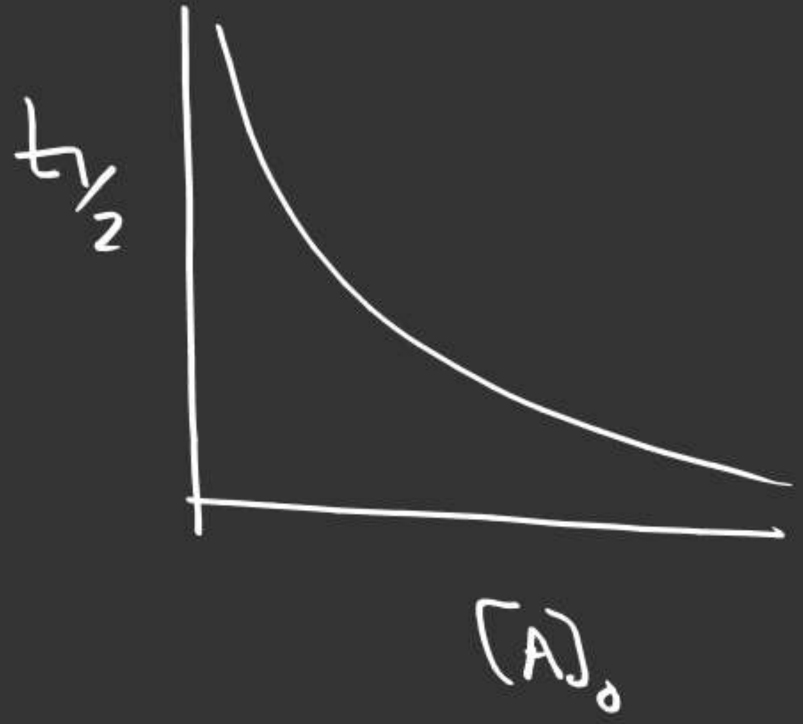




$$-\frac{d[A]}{dt} = k[A]^2$$

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

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



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Case-II If two reactants are involved :→

Cond^n-I order wrt each is one

Cond^n-II stoichiometric coeff are same for both reactants

(a) for same initial conc

$$A + B \longrightarrow \text{Product}$$

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

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

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

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(b) for different initial conc.

$$A + B \longrightarrow \text{Product}$$

$$a-x \qquad b-x$$

$$\left(-\frac{d[A]}{dt}\right) = k[A][B]$$

$$-\frac{d(a-x)}{dt} = k(a-x)(b-\cancel{x})$$

$$\frac{1}{(b-a)}\int \frac{(b-\cancel{x})-(a-x)}{(a-x)(b-x)}dx = k\int dt$$

$$\frac{1}{b-a}\left[\int_0^x \frac{dx}{a-x} - \int \frac{dx}{b-x}\right] = kt$$

$$\frac{1}{b-\cancel{a}}\left[\ln \frac{a}{(a-x)} \cdot \frac{(b-\cancel{x})}{b}\right] = kt$$

$$b >> a > x$$

$$\ln \frac{a}{a-x} = (bk)\,t$$

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

Pseudo 1st order Rxn

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

$0.001 \quad\quad 1$

$$A + B$$

$500 - x \quad 1000 - x$

order = 3

if $[B] >> [A]$ order = 2 $\quad -\frac{d[A]}{dt} = k'[A]^2$

if $[A] >> [B]$ order = 1 $\quad -\frac{d[A]}{dt} = k''[B]$

if conc of both [A] & [B] are very large order = 3

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n^{th} order Rxn

$$pA \longrightarrow \text{Product}$$

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

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

$$\frac{1}{(n-1)}\left[\underbrace{\frac{1}{[A]_t^{n-1}}} - \frac{1}{[A]_0^{n-1}}\right] = kt$$

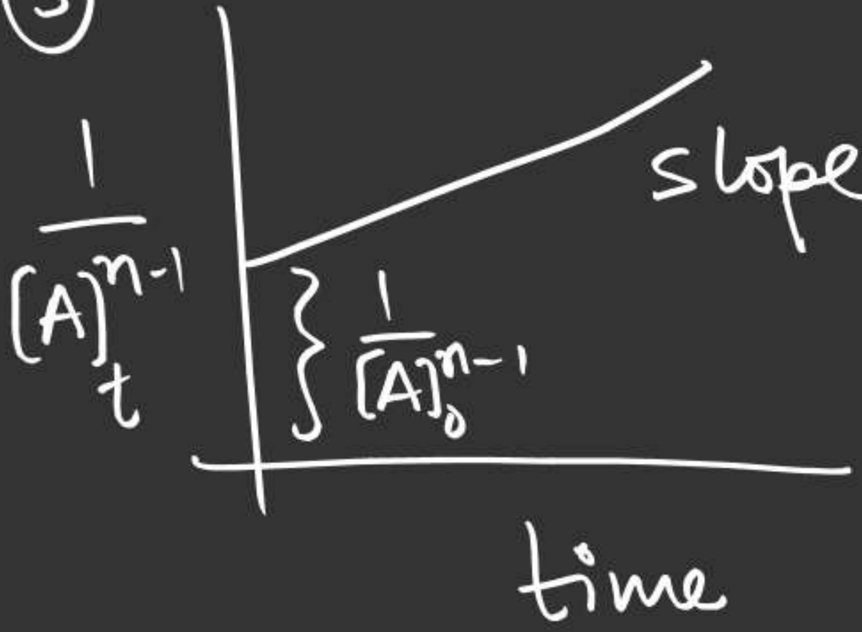
① Completion time

$n \geq 1$ completion time $= \infty$

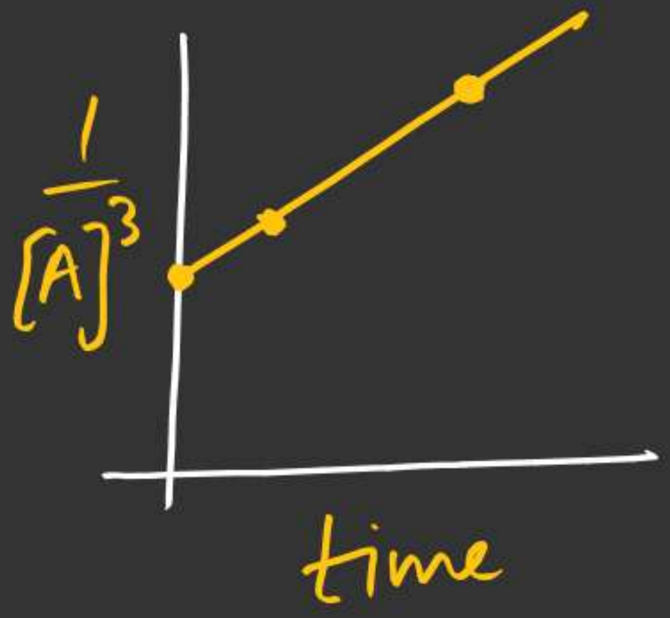
② $t_{1/2} = \frac{1}{(n-1)} \frac{2^{n-1}-1}{[A]_0^{n-1}} \times \frac{1}{k}$

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

③



slope $= (n-1)k$



order $= 4$

$n-1 = 3$

$n = 4$

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Exp. determination of order of Rxn.

① Hit & trial method

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

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

$$\boxed{\text{O-I} \quad 31-41}$$

② $t_{1/2}$ method

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

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left\{\frac{[A_0]_1}{[A_0]_2}\right\}^{n-1}$$

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6 $\quad 2Cu_{(s)} + H_2O \longrightarrow Cu_2O(s) + H_2$ $\quad \Delta G^\circ = 10^5$

$= -RT \ln K_p$

$$K_p = \frac{P_{H_2}}{P_{H_2O}} = \frac{P_{H_2}}{10^{-2}}$$

$$P_{H_2} = 10^{3} \text{ bar}$$

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8

$$\begin{tikzcd}
C(\text{graphite}, 298K, P) \arrow[r, "\Delta G = 0"] & C(\text{diamond}, 298K, P) \arrow[d, "= V_d(1-P)"] \\
C(\text{graphite}, 298, 1\text{bar}) \arrow[u, "\Delta G = V_g(P-1)"] \arrow[r] & C(\text{diamond}, 298, 1\text{bar})
\end{tikzcd}$$

$$\Delta G^\circ_r = 2.9\ kJ - 0$$
$$= 2900\ J$$

$$2900 = V_g(P-1) + 0 + V_d(1-P)$$

$$2900 = (P-1)(V_g - V_d)$$

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2017 Q.9

endo $T \uparrow$ $K_{eq} \uparrow$ forward ΔS_{sys}

exo $T \uparrow$ $K_{eq} \downarrow$

$$\Delta S_{surr} = \frac{q_{surr}}{T}$$

$$= \frac{-q_{sys}}{T}$$

$$= \frac{-\Delta H_{sys}}{T}$$

ΔS_{surr}