Q. For Rxn $A(g) \longrightarrow 3B(g) + C(g)$

Pressure at start and after 20 min. are 100 mmHg and 150 mm Hg respectively. Find 'k' for 1st order. ($\ln 2 = 0.7$)

Sol.

$$A(g) \longrightarrow 3B(g) + C(g)$$

	$A(g)$	$3B(g)$	$C(g)$
$t = 0$	100 mm	—	–
$t = 20$ min	$(100 - p)$	$3p$	p

$$(100 - \cancel{p}) + 3p + \cancel{p} = 150$$

$$100 + 3p = 150$$

$$p = 50/3$$

$$K = \frac{1}{t} \ln \frac{100}{100 - p}$$

$$K = \frac{1}{20} \ln \frac{100}{100 - 50/3}$$

$$K = \frac{1}{20} \ln \frac{300}{250}$$

$$K = \frac{1}{20} \ln\left(\frac{6}{5}\right) \text{ min}^{-1}$$

Q. $A(g) \longrightarrow 2B(g) + C(g)$

For 1st order

time (sec)	2.303	∞
Total Pressure	200 mm	300 mm

Find 'K' for 1st order.

Sol.

	$A(g) \longrightarrow$	$2B(g)$	$+ C(g)$
$t=0$	P_0	—	—
$t=t$	$P_0 - p$	$2p$	p
$t=\infty$	—	$2P_0$	P_0

$$2P_0 + P_0 = 300$$

$$P_0 = 100 \text{ mm}$$

$$(P_0 - \not{p}) + 2p + \not{p} = 200$$

$$100 + 2p = 200$$

$$p = 50 \text{ mm Hg}$$

$$K = \frac{1}{t} \ln \frac{P_0}{P_0 - p}$$

$$K = \frac{1}{2.303} \ln \frac{100}{100 - 50}$$

$$K = \frac{2.303}{2.303} \log 2$$

$$K = \log 2 \text{ sec}^{-1}$$

Note :- If in question (P_0, P_t, P_∞) all are given, then inert gas presence may be there.

Case - 4

$$A(g) \longrightarrow B(g) + C(g)$$

time	0	t	∞
Total Pressure	P_0	P_t	P_∞

Cal. 'K'

Sol.

	$A(g)$	$\longrightarrow B(g)$	$+ C(g)$
$t=0$	P_A	–	–
$t=t$	$P_A - p$	p	p
$t=\infty$	–	P_A	P_A

$$K = \frac{1}{t} \ln \frac{P_A}{P_A - p}$$

$$P_A + P_{inert} = P_0 \quad \text{—— (1)}$$

$$(P_A - p) + p + p + P_{inert} = P_t \quad \text{—— (2)}$$

$$- \; + P_A + P_A + P_{inert} = P_\infty \quad \text{—— (3)}$$

(3) − (1) $\quad P_A = (P_\infty - P_0)$

(3) − (2) $\quad (P_A - p) = (P_\infty - P_t)$

$$K = \frac{1}{t} \ln \left(\frac{P_\infty - P_0}{P_\infty - P_t} \right)$$

Q

$$AB(g) \longrightarrow A(g) + B(g) + 2C(s)$$

time (sec.)	0	t	∞
Total Pressure (mm Hg)	200	342.5	390

Cal. 't' if $k = 0.001\ sec^{-1}$ for 1st order ($\ln 2 = 0.7$)

Sol:

$$AB(g) \longrightarrow A(g) + B(g) + 2C(s)$$

	$AB(g)$	$A(g)$	$B(g)$	$2C(s)$
$t=0$	P_A	—	—	—
$t=t$	$P_A - p$	p	p	—
$t=\infty$	—	P_A	P_A	—

$$P_A + P_{inert} = 200 \quad —(1)$$

$$(P_A - p) + p + p + P_{inert} = 342.5 \quad —(2)$$

$$P_A + P_A + P_{inert} = 390 \quad —(3)$$

(3) − (1) $\quad P_A = 390 - 200 = 190$ mm Hg

(3) − (2) $\quad (P_A - p) = 390 - 342.5 = 47.5$ mm Hg

$$k = \frac{1}{t} \ln\left(\frac{P_A}{P_A - p}\right)$$

$$0.001 = \frac{1}{t} \ln \frac{190}{47.5}$$

$$0.001 \times t = 2 \ln 2$$

$$t = 1400\ sec.$$

H.W.

S-I 9, 14, 22, 31, 33, 36

S-2 1, 2, 8

O-I 39, 40

O-II 5, 6, 7

J-Mains → 1, 2, 5, 6, 9, 12, 13, 14,

S.I

33.

$$A \longrightarrow B + C + D$$

	A	B	C	D	
$t=0$	P_0	-	-	-	$\rightarrow P_0$
$t=t$	$P_0 - p$	p	p	p	$\rightarrow P_0 + 2p$
$t=\infty$	-	P_0	P_0	P_0	$\rightarrow 3P_0$

$(P\uparrow)$ at $(t=t)$ $\quad [(P_0+2p) - P_0] = 540$

$$2p = 540$$

$$p = 270$$

$(P\uparrow$ at $t=\infty)$ $\quad [3P_0 - P_0] = 600$

$$P_0 = 300$$

$$K = \frac{1}{200} \ln\left(\frac{300}{300-270}\right)$$

36.

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

	$2N_2O_5$	$4NO_2$	O_2
$t=0$	P_0	–	–
$t=t$	$P_0 - p$	$2p$	$p/2$
$t=\infty$	–	$2P_0$	$\frac{P_0}{2}$

$(t=\infty)$ $\left(2P_0 + \frac{P_0}{2}\right) = 500 \Rightarrow P_0 = ?$

$(t=t)$ $(P_0 - p) + 2p + \frac{p}{2} = 300 \Rightarrow p = ?$

(14)

$$2NH_3 \longrightarrow N_2 + 3H_2$$

	$2NH_3$	N_2	$3H_2$
$t=0$	3 atm	—	—
$t=10$ sec.	$(3-p)$	$\frac{p}{2}$	$\frac{3p}{2}$

$R = 0.1 = K_{rxn}$

$K_{rxn} = 0.1$ atm/sec.

$K_{rxn} = \frac{K_{diss}}{2}$

$0.1 = \frac{K_{diss}}{2}$

$K_{diss} = 0.2$

$(A_0 - A_t = Kt)$

$3 - (3-p) = 0.2 \times 10$

$p = 2$

Total Press. $\Rightarrow (3-p) + \frac{p}{2} + \frac{3p}{2}$

$= (3+p) = 5$

S.2

① $2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$

	P	Q	R	S
$t=0$	P_0	–	–	–
$t=t$	$P_0 - p$	$2p$	$\frac{p}{2}$	–
$t=\infty$	–	$2P_0$	$\frac{P_0}{2}$	–

$$\left(2P_0 + \frac{P_0}{2}\right) + (V.P.)_S = 617$$

$$\frac{5P_0}{2} + 32.5 = 617 \quad (P_0 = ?)$$

$$(P_0 - p) + 2p + \frac{p}{2} + 32.5 = 317 \quad (p = ?)$$

$$K = \frac{1}{30} \ln\left(\frac{P_0}{P_0 - p}\right)$$

S.2/2 (Class Discussion)

(Pseudo-order Rxn)

S-I 19.

$$A + 2B \longrightarrow C + D$$

	A	2B	C	D
t=0	0.6	0.8	–	–
t=t	0.6 − p	(0.8 − 2p)	p	

(p = 0.2) → Given

(0.6 − 0.2) = 0.4

(0.8 − 2×0.2) = 0.4

$$R = K(A)^1 (B)^2$$

$$R = K(0.6)(0.8)^2$$

$$R' = K(0.4)(0.4)^2$$

$$\frac{R'}{R} = ?$$

A → P

$$R = K(A)^1$$

$\frac{0-2}{⑤}$

$$R = k_3 (R-u)(x^{\cdot})$$

$$\frac{k_1}{k_2} = \frac{(x^{\cdot})^2}{x_2}$$

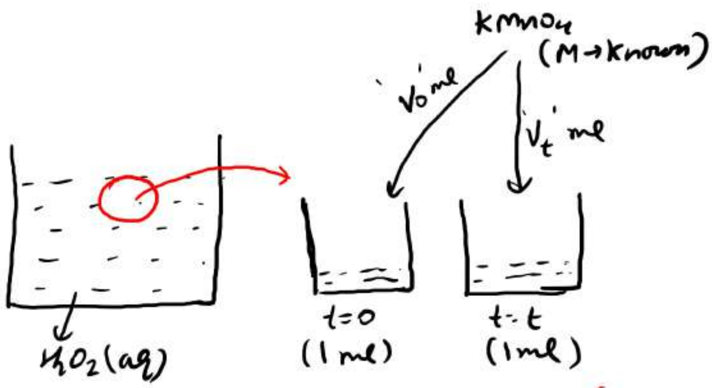
$$x^{\cdot} = \left(\frac{k_1}{k_2}\right)^{1/2} x_2^{1/2}$$

$$R = k_3 (R-u) \cdot \left(\frac{k_1}{k_2}\right)^{1/2} x_2^{1/2}$$

$$R = k_3 \left(\frac{k_1}{k_2}\right)^{1/2} \cdot (R-u)(x_2)^{1/2}$$

Problems related to titration :- (In terms of Volume of Reagent)

Case-1 Decomposition of H_2O_2 (aq) :-



$H_2O_2 \propto a$ $\qquad$ $H_2O_2 \propto (a-x)$

$$H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$$

	H_2O_2	H_2O	O_2
t=0	a	–	–
t=t	(a-x)	x	x/2

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

(nf=2) (nf=5)

$$H_2O_2^{-1} + KMnO_4 \longrightarrow Mn^{+2} + \overset{0}{O_2}$$

t=0 $\quad$ Eq of H_2O_2 = Eq of $KMnO_4$

$$a \times 2 = M \times V_0 \times 5$$

t=t

$$(a-x) \times 2 = M \times V_t \times 5$$

$$\left(\frac{a}{a-x}\right) = \frac{V_0}{V_t}$$

$$\boxed{K = \frac{2.303}{t}\log\left(\frac{V_0}{V_t}\right)}$$

Eq = mole × nf

Eq = N × V → N = M × nf

$V_0 \longrightarrow$ volume of $KMnO_4$ consumed with H_2O_2 at $t=0$

$V_t \longrightarrow$ " " " " " " " $t=t$

In such titration, a fixed amount of H_2O_2 sample is taken at different interval of time and titrated with oxidising agent ($KMnO_4$), whose molarity is known.

Question

Time (min)	0	10	20
Volume of $KMnO_4$ (ml)	22.8	13.3	8.25

In H_2O_2 & $KMnO_4$ titration. Calculate 'k'

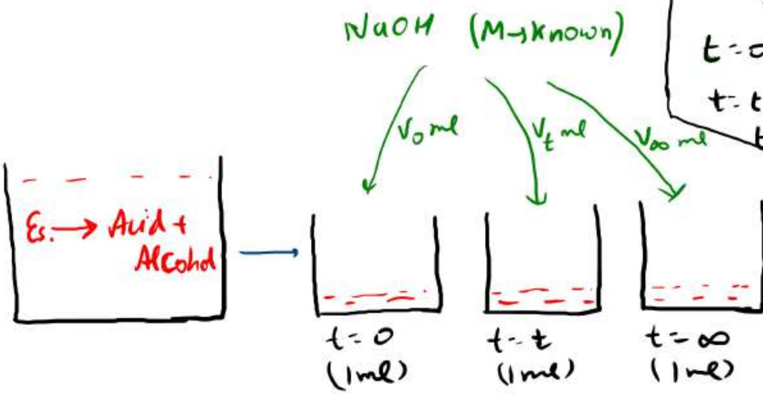
Sol. $K = \frac{2.303}{10} \log \frac{22.8}{13.3}$ ✓ or $K = \frac{2.303}{20} \log \frac{22.8}{8.25}$

Case - 2   Hydrolysis of Ester in Acidic Medium :-

$$CH_3COOC_2H_5(aq) + H_2O(l) \xrightarrow{H^+} CH_3COOH(aq) + C_2H_5OH(aq)$$

	$CH_3COOC_2H_5$	CH_3COOH	C_2H_5OH
t = 0	a	—	—
t = t	a − x	x	x
t = ∞	—	a	a

$$K = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$



t = 0: $V_0 \propto [H^+]_{catalyst}$ —— ①

t = t: $V_t \propto x + [H^+]_{catalyst}$ —— ②

t = ∞: $V_\infty \propto a + [H^+]_{catalyst}$ —— ③

③ − ①: $a \propto (V_\infty - V_0)$

③ − ②: $(a - x) \propto (V_\infty - V_t)$

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

V_0, V_t & V_∞ are Volume of NaOH which is used in titration at t = 0, t = t & t = ∞

① Hydrolysis of Ester follow 1st order kinetics.

② To study it's Kinetics, we take a fixed amount of sample at different interval time and titrate it with strong base (like NaOH), whose Molarity was known.

③ NaOH used reacts with acid formed and (H^+) ion present due to catalyst

Q. Consider following data taken during hydrolysis of ester

time (sec.)	0	60	∞
Volume of NaOH (ml)	30	40	50

Calculate time in which volume of NaOH used is 47.5 ml ?

Sol.

$$K = \frac{1}{t} \ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

$$K = \frac{1}{60} \ln\left(\frac{50-30}{50-40}\right)$$

$$K = \frac{\ln 2}{60}$$

$$K = \frac{1}{t} \ln\left(\frac{50-30}{50-47.5}\right)$$

$$\frac{\ln 2}{60} = \frac{1}{t} \ln\left(\frac{20}{2.5}\right)$$

$$\frac{\ln 2}{60} = \frac{1}{t} \ln 8$$

$$t = 180\ \text{sec}$$

Note

Hydrolysis of Ester $\longrightarrow$ (Pseudo Order Rxn)

$$Ester + H_2O(l) \xrightarrow{[H^+]} Acid + Alcohol$$

$$R = K[Ester]^1[H_2O]^1[H^+]^1$$

$[H_2O]$ (Excess) $\longrightarrow$ constant

$$R = K'[Ester]^1[H^+]^1$$

where $K' = K[H_2O]^1$

During a progress of Rxn, $[H^+]_{catalyst} \longrightarrow$ Const.

$$\boxed{R = K''[Ester]^1}$$

where $K'' = K'[H^+]_{cat.}$

S-I/39

$$R = K[Ester]^1[H^+]^1[H_2O]^1$$

$[H^+]$ (1.8M), $[H_2O]$ (55.55M)

$$R = K'(Ester)^1$$

$K' = K[H^+][H_2O]$

$= (1.386 \times 10^{-3}) \times 1.8 \times 55.55$ → 100

$K' = 0.1386$

$t_{1/2} = \frac{\ln 2}{K'} = \frac{0.693}{0.1386}$ min.

H.W.

S-I 34, 39, 40

O-I 56, 57

O-2 14, 15, 16, 17

J.M. 1, 2, 5, 6, 9, 12, 13, 14

M.t.2.

S-I 34, 39, 40

O-I 56, 57

O-2 14, 15, 16, 17

J.M. 1, 2, 5, 6, 9, 12, 13, 14

Sol. J.M. – 5

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

$$\begin{array}{lll} 50 & - & - \\ 50-p & 2p & p/2 \end{array}$$

$$\left(50 - p + 2p + \frac{p}{2}\right) = 87.5$$

$$p = 25$$

$$K = \frac{1}{t} \ln \frac{50}{50-p}$$

$$K = \frac{1}{30} \ln \frac{50}{50-25}$$

$$K = \frac{1}{60} \ln \frac{50}{50-p'}$$

$$\frac{1}{30} \ln 2 = \frac{1}{60} \ln \frac{50}{50-p'}$$

$$\ln 4 = \ln \frac{50}{50-p'} \Rightarrow p' = ?$$

Total Press. (at 60 min)

$$\left[(50 - p') + 2p' + \frac{p'}{2}\right]$$

(2)

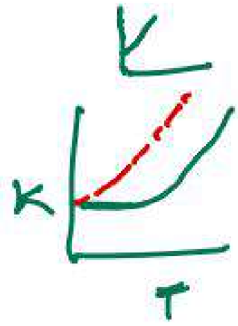
$$K_1 = A e^{-Ea_1/RT}$$

$$K_2 = A e^{-Ea_2/RT}$$

$$K_2 = A e^{-2Ea_1/RT}$$

$$K_2 = \left(A e^{-Ea_1/RT}\right) \times e^{-Ea_1/RT}$$

$$K_2 = K_1 e^{-Ea_1/RT}$$



(12)

$$R = K (P_A)^n$$

$$1 = K \left(363 \times \frac{95}{100}\right)^n$$

$$0.5 = K \left(363 \times \frac{67}{100}\right)^n$$

$$\frac{1}{0.5} = \frac{(95/100)^n}{(67/100)^n}$$

$$2 = (1.414)^n$$

$$\Rightarrow n = 3$$

(1)

10°C ⟶ Rate double

0°C ⟶ R

10°C ⟶ 2R

20°C ⟶ (2R) × 2

30°C ⟶ (4R) × 2

J.M/21

$\ln k$ vs $\frac{1}{T}$

$$\text{slope} = -\frac{E_a}{R} = -4606$$

$$K_1 = 10^{-5} \rightarrow T_1 = 400K$$

$$K_2 = ? \rightarrow T_2 = 500K$$

$$\ln\left(\frac{K_2}{10^{-5}}\right) = 4606\left(\frac{1}{400} - \frac{1}{500}\right)$$

$$\log\left(\frac{K_2}{10^{-5}}\right) = \frac{4606}{2.303}\left(\frac{1}{400} - \frac{1}{500}\right)$$

$$\ln\left(\frac{K_2}{10^{-5}}\right) = 2000 \times \frac{100}{400 \times 500}$$

$$\ln\left(\frac{K_2}{10^{-5}}\right) = 1$$

$$K_2 = 10^{-5} \times 10$$

J.M/6.

$$E_{af} - E_{ab} = -40$$

$$\frac{E_{af}}{E_{ab}} = \frac{2}{3}$$

(13)

$$\frac{\ln 2}{10} = \frac{1}{t}\ln\frac{a}{3a/4}$$

$$t = ?$$

J.M/g.

$$\ln k = \ln A - \frac{E_a}{RT}$$

R_1 $$\ln k_1 = \ln A - \frac{E_{a1}}{RT}$$

R_2 $$\ln k_2 = \ln A - \frac{E_{a2}}{RT}$$

$$\ln \frac{k_2}{k_1} = \frac{E_{a1} - E_{a2}}{RT} = \frac{10}{\frac{8.314}{1000} \times 300}$$