HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

1. $aA + bB \longrightarrow \text{Product}$

$$\frac{dx}{dt} = k[A]^a[B]^b$$

(i) As on doubling concentration of A rate become four time so a = 2.
(ii) On four time concentration of B rate become double

so $b = \frac{1}{2}$.

So, Given equation : $2a + \frac{1}{2}b \longrightarrow \text{Product}$

$$-\frac{1}{2}\frac{d[A]}{dt} = -2\frac{d[B]}{dt} \Rightarrow -\frac{d[A]}{dt} = -4\frac{d[B]}{dt}$$

2. $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

$$\text{Rate} = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{1}{2}\frac{d[H_2]}{dt} = \frac{d[N_2]}{dt}$$

$$= \frac{1}{2}\frac{d[H_2O]}{dt} = K_1[NO][H_2]$$

(1) $\frac{d[H_2O]}{dt} = 2K_1[NO][H_2] = K[NO][H_2]$

So **k = 2k1**

(2) $-\frac{d[NO]}{dt} = 2k_1[NO][H_2] = K_1'[NO][H_2]$

k1' = 2k1

(3) $-\frac{d[H_2]}{dt} = 2k_1[NO][H_2] = K_1''[NO][H_2]$

k1" = 2K1

4. $xA \longrightarrow yB$

$$\frac{-1}{x}\frac{d}{dt}[A] = \frac{1}{y}\frac{d}{dt}[B] \Rightarrow \frac{-d}{dt}[A] = \frac{x}{y}\frac{d}{dt}[B]$$

$$\log\left(\frac{-d[A]}{dt}\right) = \log\left(\frac{x}{y}\right)\left(\frac{+d[B]}{dt}\right)$$

$$\Rightarrow \log\frac{-d}{dt}[A] = \log\frac{d}{dt}[B] + \log\left(\frac{x}{y}\right)$$

$$\log\left(\frac{x}{y}\right) = 0.3 \Rightarrow \frac{x}{y} = \frac{2}{1} \Rightarrow x:y::2:1$$

5. $\frac{d}{dt}[SO_3] = 100\,\text{gram/min} = \frac{100}{80}\,\text{mole/min} = 1.25\,\text{mole/min}.$

$$\frac{-1}{2}\frac{d}{dt}[SO_2] = \frac{-d}{dt}[O_2] = \frac{1}{2}\frac{d}{dt}[SO_3]$$

$$\frac{-d}{dt}[O_2] = \frac{1.25}{2}\,\text{mole/min} = \frac{1.25}{2}\times 32\,\text{gram/min}$$

= 20 gram/min

8. $A + B \longrightarrow \text{product}$

$r = K[A]^1[B]^2$

$r_1 = K[1]^1\,[1]^2 = 1\times10^{-2} \quad (K = 1\times10^{-2})$

$$r_1 = K\left[\frac{1}{2}\right]\left[\frac{1}{2}\right]^2 = 1\times10^{-2}\times\frac{1}{8} = 1.25\times10^{-3}$$

10. $2A + B \longrightarrow \text{product}$

$$-\frac{d[A]}{dt} = K[A] \Rightarrow -\frac{d[A]}{dt} = K[a-x]$$

$$C_t = C_0e^{-Kt} \Rightarrow C_t = C_0e^{-K\times\frac{1}{K}}$$

$$C_t = C_0e^{-1} \Rightarrow C_t = \frac{C_0}{e}$$

11. $C_t = C_0e^{-Kt}$

According to question

$C_{A,t} = C_{B,t}$

$C_A\,e^{-K_At} = C_B\,e^{-K_Bt}$

$$\frac{C_A}{C_B} = \frac{e^{-K_Bt}}{e^{-K_At}} \Rightarrow \frac{C_A}{C_B} = e^{(K_A-K_B)t}$$

$$4 = e^{\left[\frac{\ln2}{5}-\frac{\ln2}{15}\right]\times t} \Rightarrow \ln4 = \left[\frac{\ln2}{5}-\frac{\ln2}{15}\right]t$$

$$\ln(2)^2 = \left[\frac{\ln2}{5}-\frac{\ln2}{15}\right]t$$

$$2\ln2 = \left[\frac{\ln2}{5}-\frac{\ln2}{15}\right]t$$

$$2 = \left[\frac{1}{5}-\frac{1}{15}\right]t \Rightarrow 2 = \frac{2}{15}\times t \Rightarrow \mathbf{t = 15\ minute.}$$

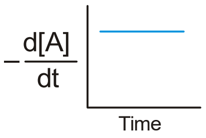
13. time Total for drop to disappears $(a_o - a_t) = kt$

$a_t = 0$

$$\frac{3.0\times10^{-6}}{(0.05\times10^{-3})\times1.0\times10^{7}} = t_{100\%} \Rightarrow t_{100\%} = 6\times10^{-9}\ \text{sec}$$

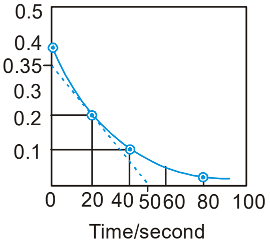
14. From given graph $x = Kt$

i.e. it is a zero order reaction.



$$\therefore\ -\frac{d[A]}{dt} = K$$

15. slope of graph at 20 sec $= \frac{dy}{dx} = \frac{0.35}{50} = 7\times10^{-3}$



17.

$$\begin{array}{lccc} & A & + \quad B & \longrightarrow \quad C \\ t=0 & a=0.1\ M & b=0.2\ M & 0 \\ t=100s & a-x & b-x & x \end{array}$$

From question, $r = k[A][B]$ and hence

$$kt = \frac{1}{b-a}\ln\frac{a(b-x)}{b(a-x)}$$

or $$10^{-3}\times100 = \frac{1}{0.2-0.1}\times2.303\times\log\frac{0.1(0.2-x)}{0.2(0.1-x)}$$

$x \approx 0.002$

$\therefore\ [A] = 0.1 - x = 0.098\ M$

19.

$$\begin{array}{lcc} & A & \rightarrow\ nB \\ t=0 & A_0 & 0 \\ t=t & A_0-x & nx \end{array}$$

From graph

$$A_0 - x = nx \Rightarrow x = \frac{A_0}{n+1}$$

$$\Rightarrow |B| = \frac{n|A_0|}{n+1}$$

20. $$\frac{1}{C_t} = \frac{1}{C_0} + Kt.$$

$$\Rightarrow \frac{1}{0.04} = \frac{1}{0.2} + 0.002\times t.$$

$$\Rightarrow 25 = 5 + 0.002\times t \Rightarrow t = \frac{20}{2\times10^{-3}} = \mathbf{10{,}000\ sec}.$$

23. $$\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1}-1}{4^{n-1}-1} \Rightarrow \frac{t_{3/4}}{t_{1/2}} = \frac{4^{n-1}-1}{2^{n-1}-1} = \frac{4^2-1}{2^2-1} = \frac{15}{3} = 5:1$$

$$\Rightarrow t_{1/2} = \frac{2^{n-1}-1}{|A|_0^{n-1}K^{(n-1)}}$$

$$\Rightarrow t_{3/4} = \frac{4^{n-1}-1}{|A|_0^{n-1}K^{(n-1)}}.$$

25. Let $r = (A)^x(B)^y$

$$x = \frac{\log\left(\frac{r_1}{r_2}\right)}{\log\left(\frac{a_1}{a_2}\right)} = \frac{\log\frac{0.1}{0.1}}{\log\left(\frac{0.012}{0.024}\right)} = \frac{\log\left(\frac{1}{8}\right)}{\log\left(\frac{1}{2}\right)}$$

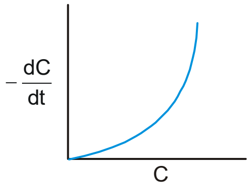
x = 3

$$y = \frac{\log\frac{r_1}{r_3}}{\log\left(\frac{b_1}{b_2}\right)} = \frac{\log\left(\frac{0.1}{0.1}\right)}{\log\left(\frac{0.035}{0.070}\right)} = \frac{\log(1)}{\log\left(\frac{1}{2}\right)}$$

y = 0

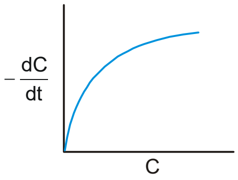
26. dt is parabolic graph

of $y = x^2$



So This the graph of second order

$y^2 = x$ $\qquad y = (x)\,\frac{1}{2}$



$$\frac{-dc}{dt} = K\,[C]^{\frac{1}{2}}$$ So reaction is $\left(\frac{1}{2}\right)$ order.

28.

Initial pressure	65	105	y	185
Halflife	290	x	670	820

Initial pressure of gas a Initial moles of gas in above question.

Half life a Initial pressure

So, it must be zero order reaction

$$t_{1/2} = \frac{C_O}{2k} = \frac{P_O}{2k} \Rightarrow 290 = \frac{65}{2\,k} \quad \Rightarrow \quad k = \frac{65}{2 \times 290}$$

$= 0.112$ mm of Hg/sec

$$x = \frac{105 \times 2 \times 290}{2 \times 65} = \mathbf{468\ sec}$$

$$670 = \frac{y \times 2 \times 290}{2 \times 64}$$

$\Rightarrow \quad y =$ **150 mm of Hg**

29. $NH_4NO_2\,(aq) \longrightarrow N_2\,(g) + 2H_2O\,(\bullet)$

$$K = \frac{2.303}{t} \log \left(\frac{V_\infty - V_O}{V_\infty - V_t}\right) \Rightarrow V_0 = 0$$

$$\Rightarrow \quad K = \frac{2.303}{20} \log \left(\frac{70 - 0}{70 - 40}\right)$$

$$\Rightarrow \quad \frac{2.303}{20} \log \left(\frac{70}{30}\right) \Rightarrow \quad K = \frac{2.303}{1200} \log \frac{7}{3}.$$

31. $A\,(s) \longrightarrow 2\,B\,(g) + C\,(g)$

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

$P_0 = 0 \quad P_t = 150 \quad P_\infty = 225$

$$\frac{1}{20} \ln \left[\frac{225}{225 - 150}\right] \Rightarrow \frac{1}{20} \ln \left(\frac{225}{75}\right) = 0.05 \ln 3$$

$$\frac{1}{20} \ln \left(\frac{225}{75}\right) = \frac{1}{20} \ln \left(\frac{225}{225 \times P_{40}}\right)$$

$$\Rightarrow \left(\frac{225}{75}\right)^2 = \frac{225}{225 \times P_{40}}$$

$$\frac{225}{75 \times 75} = \frac{1}{225 - P_{40}} \Rightarrow$$ **P40 = 200**

33. $k\,t = \text{In}\left(\frac{C_O}{C_t}\right)$

	$2\,N_2O_5$	$\longrightarrow$	$2N_2O_4$	+	O_2
t=0	200 cm^3		0		0
t=t	20 cm^3		180cm^3		90 cm^3
t=∞	0		200cm^3		100 cm^3

Initial volume of N_2O_5 = 200 cm^3.

because Max. volume of O_2 = 100 cm^3.

$$\therefore \quad K \times 500 = \text{In}\left(\frac{200}{20}\right) \Rightarrow k = \frac{\text{In}\,10}{500} = \frac{2.303}{500}.$$

36. $$K = \frac{1}{10 \times 60} \ln \frac{r_\infty - r_0}{r_\infty - r_t} = \frac{1}{10 \times 60} \ln \frac{-10 - 40}{-10 - 15}$$

$$= \frac{1}{10 \times 60} \times \ln 2 = \frac{0.0693}{60} = 1.15 \times 10^{-3}\ \text{sec}^{-1}.$$

38. $$\%\ \text{of}\ B = \frac{k_1 \times 100}{k_1 + k_2} = \frac{1.26 \times 10^{-4} \times 100}{12.6 \times 10^{-5} + 3.8 \times 10^{-5}} = 76.83\%.$$

$$\%\ \text{of}\ C = \frac{k_2 \times 100}{k_1 + k_2} = \frac{3.8 \times 10^{-5} \times 100}{12.6 \times 10^{-5} + 3.8 \times 10^{-5}} = 23.17\%$$

39. $[B] + [C] = 2\ M$

$$\frac{[B]}{[C]} = \frac{2k_1}{3k_2} = \frac{4}{9}$$

42. $A + B \rightleftharpoons C + D$

$$\left[\frac{dx}{dt}\right] = 0$$

$k_1\,[A]\,[B] - k_2[C]\,[D] = 0$

$k_1\,[A]\,[B] = k_2[C]\,[D]$

$[A]\,[B] = [C]\,[D]$

$0.4 \times 0.25 = 0.2 \times 0.5$

1 = 1.

44. Equation : $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2{}^+]$

Given, $\frac{dx}{dt} = 2 \times 10^7\ L^2\,mol^{-2}\,s^{-1}\,[Ag^+]\,[NH_3]^2$

$- 1 \times 10^{-2}\,s^{-1}\,[Ag(NH_3)_2{}^+]$

For equilibrium $\frac{dx}{dt} = 0$

$2 \times 10^7\,[Ag^+]\,[NH_3]^2 - 1 \times 10^{-2}\,[Ag(NH_3)_2{}^+] = 0$

$$\frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2} = \frac{2 \times 10^7}{1 \times 10^{-2}} = 2 \times 10^9\ L^2\,mol^{-2}.$$

45. $K_1 = A_1 e^{-E_1/RT}$ and $K_2 = A_2 e^{-E_2/RT}$

$$\frac{K_1}{K_2} = \frac{A_1}{A_2} = e^{(E_2-E_1)/RT}$$; A_1 and A_2 are not given.

46. $$\log K = \left[\frac{-E_a}{2.303R}\right] \times \frac{1}{T} \quad + \log A$$

at Y axies

$$\left[\frac{1}{T}\right] = 0 T = \infty$$

at x axis

$$\log k = 0 \ \frac{-E_a}{2.303R} \times \frac{1}{T} = -\log A \ \Rightarrow \ \frac{E_a}{R \ln A} = T$$

50. For reaction, $A \longrightarrow B$.

$E_a = 10$ kJ/mole , $\Delta H = 5$ kJ/mole

Rxn endothermic because $\Delta H\ (+)$

$\Delta H = E_a - E_b$

$5 = 10 - E_b$

$E_{ab} = 10 - 5 = 5$ kJ/mole. Then [B].

51. $$\frac{k_t}{k_0} = (TC)^{t-0/10}$$

Taking log gives $\log_e k_t - \log_e k_0 = \frac{t}{10} \log_e (TC)$

$$\Rightarrow \ \ln k_t = \ln k_0 + \left(\frac{\ln (TC)}{10}\right) t$$

Comparision indicates $\ln (TC) = \ln 3 \Rightarrow TC = 3$

53. $$\log k = -\frac{E_a}{2.303\ R}\ \frac{1}{T} + \text{constant}$$

$$= -\frac{E_a}{2.303\ R} \times 10^{-3} \times \frac{10^3}{T} + \text{constant}$$

thus, slope of graph will be $-\dfrac{E_a \times 10^{-3}}{2.303\ R} = -\dfrac{4}{0.4}$

$\Rightarrow E_a = 2.303 \times 1.98 \times 10^4 = 45600$ cal

56. $A + A \xrightarrow{K_1} A + A^*$ $\quad A^* + A \xrightarrow{K_2} 2A$

Rate of decomposition

$A = K_1[A]^2$

Rate of formation $A = K_2[A]\,[A^*]$

At equilibrium rate of decomposition = rate of formation

$$K_1[A]^2 = K_2[A][A^*]$$

$$[A^*] = \frac{K_1}{K_2}[A]$$

58. For Rxn rate determining step is slowest step

Then in 1st Rxn

$\text{Rate} = k\,[NO_2]\,[O_3]$ .....(i)

But 2nd Rxn

$O_3 \underset{k_b}{\overset{k_a \text{ fast}}{\rightleftharpoons}} O_2 + [O]$ ....(a)

$NO_2 + O \xrightarrow{\text{Slow}} NO_3$ ....(b)

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$ ....(c)

Then for Rxn (a)

$$\frac{k_a}{k_b} = \frac{[O_2][O]}{[O_3]} = k_{eq}$$ ....(d)

by Rxn (b)

$\text{Rate} = k\,[NO_2]\,[O]$ ....(ii)

put value of [O] from (d) to (ii)

$$\text{Rate} = k\ \frac{k_{eq}[O_3]}{[O_2]} \times [NO_2]$$

$$\text{Rate} = \frac{k_1[NO_2][O_3]}{[O_2]}$$

59. $\text{Rate} = K\,[X][Y_2]$

$$K_{eq} = \frac{[X]^2}{[X_2]}$$

$$[X] = \sqrt{K_{eq}} \times [X_2]^{1/2}$$

$$\text{Rate} = K \times \sqrt{K_{eq}}\ [X_2]^{1/2}\,[Y_2]$$

So the order of overall reaction is 1.5

$$K_{eq} = \frac{[X]^2}{[X_2]}$$

$$[X] = \sqrt{K_{eq}} \times [X_2]^{1/2}$$

60. $$C_3 = \frac{C_0}{2^3} = \frac{C_0}{8}$$

$$\frac{C_3}{C_0} = \frac{1}{8}$$

61. $N = N_0\left(\frac{1}{2}\right)^n$

$$\left(\frac{x\,v}{20}\right) = (x) \times 200\left(\frac{1}{2}\right)^4$$

$V = 250$ ml.

So added volume of water = 50 ml.

66. $t = \frac{2.303}{\lambda}\log_{10}\left[\frac{n+n}{n}\right]$

$$t = \frac{2.303}{0.693} \times 4.5 \times 10^9 \log_{10}[2] = 4.5 \times 10^9 \text{ years}$$

68. $\lambda t = \ln\left[\frac{n_x + n_y}{n_x}\right]$

$$t = \frac{0.693 \times 10^9}{0.693} \times 2.303 \log_{10}\left[\frac{1+7}{1}\right] = 2.079 \times 10^{10} \text{ years}$$

72. As $t_{50\%}$ is constant. Hence order of reaction is 1.

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

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

73. $C_t = C_0\, e^{-Kt}$

$$\frac{1}{e^2} \times C_0 = C_0\, e^{-Kt}$$

$$e^{-2} = e^{-Kt}$$

$$t = \frac{2}{K}$$

$t = 2$ natural life time.

75.

	A(g)	+	2B(g)	→	C(g)
$t = 00.$	4 atm		1 atm		0 atm
$t = t$	(0.4–0.3)atm		(1 – 0.6)atm		0.3 atm

Since reaction is elementary.

So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient

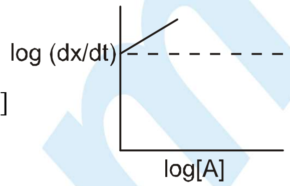
$\text{Rate} = K[A][B]^2$

$\text{Rate}_{(\text{Initial})} = K[0.4][1]^2$

$\text{Rate}_{(\text{aftar } t=t)} = K[0.1][0.4]^2$

$$\frac{R_{(t=t)}}{R_{(t=o)}} = \frac{K[0.1][0.4]^2}{K[0.4][1]} = \frac{1}{25}$$

78. $\frac{dx}{dt} = k[A]^2$



$$\log\left(\frac{dx}{dt}\right) = \log k + 2\log[A]$$

Slope = 2

Intercept= log k.

79. $nA \longrightarrow B$

a

$a–x \quad \frac{x}{n} \qquad t_{1/2} = 24$ min

$$\text{at } t = 48 \quad a–x = \frac{x}{n} \Rightarrow a = \frac{(1+n)x}{n}\ ;\ \frac{na}{1+n} = x$$

$$\frac{\ln 2}{24} = \frac{1}{48}\ \ln\frac{a}{a - \frac{na}{(1+n)}} \Rightarrow 4 = \frac{a(1+n)}{a} \Rightarrow n = 3.$$

80. If easter 50% hydrolysed then

$$x = \frac{a_0}{2} \Rightarrow (a_0 - x) = \frac{a_0}{2}$$

We can write

$a_0 \propto (V_\infty - V_0)$

$(a_0 - x) \propto (V_\infty - V_t)$

$$\frac{V_\infty - V_0}{2} = (V_\infty - V_t)$$

$$V_\infty - V_0 = 2V_\infty - 2V_t$$

$$V_t = \frac{(V_\infty - V_0)}{2}$$

or $\quad V_\infty = 2V_t - V_0$

82. Given $\quad (r_\infty - r_0) = a\ ,\ (r_\infty - r_t) = (a - x)$

At 50% Inversion

$$\frac{a}{2} = (a - x)$$

$$\frac{(r_\infty - r_0)}{2} = (r_\infty - r_t)$$

$(r_\infty - r_0) = 2r_\infty - 2r_t$

$r_0 = 2r_t - r_\infty$

85.

	$2NO_2(g)$	+	$F_2(g)$	→	$2NO_2F(g)$
$t = 0$	$2P_O$		P_O		
$t = 0$	2 atm		1 atm		0
$t = t$	0		0		2 atm

$2P_O + P_O = 3$ atm

$P_O = 1$ atm

86. $A \longrightarrow B + 2C + 3D$

	A	B	2C	3D
Optical rotation –		θ_1	θ_2	θ_3
t=0	a	0	0	0

Optical rotation at $t = 0$ is zero.

t=t	a–x	x	2x	3x

Optical rotation at time = t is $(x.\theta_1 + 2x.\theta_2 + 3x.\theta_3)$.

t=∞	0	a	2a	3a

Optical rotation at time = ∞ is $(a.\theta_1 + 2a.\theta_2 + 3a.\theta_3)$.

$(x.\theta_1 + 2x.\theta_2 + 3x.\theta_3) = r_t \quad ; \quad (a.\theta_1 + 2a.\theta_2 + 3a.\theta_3) = r_\infty$

$$x = \frac{r_t}{\theta_1 + 2\theta_2 + 3\theta_3} \quad ; \quad a = \frac{r_\infty}{\theta_1 + 2\theta_2 + 3\theta_3}$$

$$k = \frac{1}{t}\ln\left[\frac{a}{a-x}\right] = \frac{1}{t}\ln\left[\frac{r_\infty}{r_\infty - r_t}\right]$$

EXERCISE - 2

Part # I : Multiple Choice

1. $K = \dfrac{K_1K_3}{K_2}$

$$Ae^{\frac{-(E_a)_{overall}}{RT}} = \frac{A_1e^{-\frac{E_1}{RT}} \times A_3e^{-\frac{E_3}{RT}}}{A_2e^{-\frac{E_2}{RT}}}$$

$$Ae^{\frac{-(E_a)_{overall}}{RT}} = \left(\frac{A_1A_3}{A_2}\right)e^{-\frac{[E_1+E_3-E_2]}{RT}}$$

$(E_a)_{overall} = E_1 + E_3 - E_2 = 30$ KJ/mole

$$2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A^* + A \qquad \text{[Fast]}$$

$$\frac{K_1}{K_2} = \frac{[A^*][A]}{[A]^2} \text{ or } [A^*] = \frac{K_1}{K_2}[A]$$

$$\text{rate} = K_3[A^*] = \frac{K_1K_3}{K_2}[A]$$

4. $3A(g) \longrightarrow 2B(g) + 2C(g)$

	3 A(g)	2 B(g)	2C (g)
t = 0	P_0		
t = 20	$P_0 - x$	$\frac{2x}{3}$	$\frac{2x}{3}$
t = ∞		$\frac{2P_0}{3}$	$\frac{2P_0}{3}$

$$\Rightarrow \frac{4P_0}{3} = 4$$

$P_0 = 3$ atm.

$$P_0 + \frac{x}{3} = 3.5$$

$\Rightarrow t_{50\%} = 20$ is the half life.

$x = 1.5 \quad t_{75\%} = 2 \times 20 = 40$ min.

$t_{87.5\%} = 3 \times t_{50\%} = 3 \times 20 = 60$ min

$$t_{99\%} = \frac{2}{3} \times t_{99.9\%} = \frac{2}{3} \times 10 \times t_{50\%} = \frac{400}{3}$$

5.

0	30	∞
30	20	–15

$$k = \frac{1}{30}\, 2.0303 \log\frac{30-(-15)}{20-(-15)}$$

$$= \frac{1}{30}\ln\frac{45}{35}\ \text{min}^{-1}$$

$$\therefore\ t_{1/2} = \frac{30\ln 2}{\ln\frac{9}{7}} = 15 \text{ min}$$

$$\frac{1}{30}\ln\frac{45}{35}\text{min}^{-1} = \frac{1}{t}\ln\frac{45}{0-(-15)}$$

$t = 120$ min

$$\frac{30-(-15)}{x-(-15)} = 2 \text{ at half time}$$

$$\Rightarrow \frac{45}{x+15} = 2 \quad \Rightarrow \quad x + 15 = \frac{45}{2}$$

$\Rightarrow x = 22.5 - 15 = 7.5°$

7. (C) Given, $\log k\,(\text{min}^{-1}) = 5 - \frac{2000}{T\,(k)}$

Compare this with

$$\log K = \log A - \frac{E_a}{2.303\,RT(k)}$$

we find $\quad A = 1 \times 10^5$

(D) $-\frac{E_a}{2.303\,R} = -2000$

$E_a = 9.212$ k cal.

8. We know, $\quad E_a = \frac{2.303\,RT_1T_2}{(T_2 - T_1)} \log\left(\frac{k_2}{k_1}\right)$

10. $P \rightarrow y, z\,,\ Q \rightarrow x\,,\ R \rightarrow y, z.$

11. (a) $t_{1/2} \propto \frac{1}{(\text{initial conc.})^{\text{order}-1}}$

(b) $t_{avg} = \frac{t_{1/2}}{0.693}$

(c) For second order reaction $t_{1/2} = \frac{1}{KC_0}$

$$\frac{1}{C_t} = \frac{1}{C_0} + Kt$$

At $t = t_{75\%}$ $\quad C_t = \frac{C_0}{4} \Rightarrow \frac{4}{C_0} = \frac{1}{C_0} + Kt_{75\%}$

$\Rightarrow t_{75\%} = \frac{3}{C_0\,K} \Rightarrow t_{75\%} = 3 \times t_{1/2}$

12. (B) Half life period independent of conc. of Zn than order w.r.t. Zn is 1st

Rate $= k\,[Zn][H^+]^n$ we can write

by data $\quad \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[Zn]}{[Zn]}\left[\frac{1\times10^{-2}}{1\times10^{-3}}\right]^n = \frac{100}{1}$

Given $\quad n = 2$

Then $\quad$ Rate $= k\,[Zn][H^+]^2$

(C) Conc. of Zn four times and H^+ ion is halved

$$\text{Rate} = k\,[4 \times Zn]\left[\frac{H^+}{2}\right]^2$$

Rate $= k\,[Zn][H^+]^2$

Rate remains and same.

(D) Similarly if conc. of H^+ doubled and [Zn] constant

Then $\quad \text{Rate}_2 = k\,[Zn]\,[2H^+]^2$

$\text{Rate}_2 = 4\,k\,[Zn]\,[H^+]^2$

$\text{Rate}_2 = 4 \text{ x } \text{Rate}_1$

13. Use $K = Ae^{-Ea/RT}$ and $\ln k = \ln A = \frac{-E_a}{R} \times \frac{1}{T}$

$$2.303 \log K = 2.303 \log A \frac{-E_a}{R}\frac{1}{T}$$

$$\log K = \log A \frac{-E_a}{2.303R}\frac{1}{T}$$

14. Over all order of Rxn $= \left(1 - \frac{1}{2}\right) = +\frac{1}{2}$.

as SO_3 for Rate of Rxn slow down.

15. $2A \longrightarrow \text{Product}$

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

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

16.	A (aq)	$\longrightarrow$	B (aq)	+	C (aq)
t=0	a		0		0
t=t	a–x		x		x
$t=\infty$	0		a		a

$(a - x) + 2x + 3x \propto n_1$

$a + 4x \propto n_1$ .....(i)

$2a + 3a \propto n_2$

$a \propto \frac{n_2}{5}$ .....(ii)

$$k = \frac{1}{t}\ln\left[\frac{a}{a - x}\right]$$

19. $A \rightarrow B$ (uncatalysed reaction) $A \rightarrow B$

$A \xrightarrow{\text{catalyst}} B$ (catalyst reaction)

$$K = A\,e^{-E_a/RT}$$

$$K_{cat.} = A\,e^{-E_{a(cat.)}/RT}$$

$$\frac{K_{cat.}}{K} = e^{(E_a - E_a') \times \frac{1}{RT}}$$

$$\frac{K_{cat.}}{K} = e^{\frac{8.314\times10^3}{8.314\times300}} = e^{3.33} = \textbf{28 times}$$

20. We have,

$$\frac{[B]_t}{[C]_t} = \frac{4k_1}{3k_2} = \frac{16}{9}$$

so, $\frac{k_1}{k_2} = \frac{4}{3}$

Now, $k = k_1 + k_2 = [2 \times 10^{-3} + \frac{3}{4} \times 2 \times 10^{-3}]\ \text{sec}^{-1}$

$$= \frac{7}{2} \times 10^{-3}\ \text{sec}^{-1} = \frac{7 \times 10^{-3} \times 60}{2}\ \text{min}^{-1}$$

so, $T_{1/2} = \frac{\ln 2}{7 \times 30 \times 10^{-3}}\ \text{min} = \frac{693}{7 \times 30} = \mathbf{3.3\ min.}$

22. $y = \frac{k_1 a}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]$

$\frac{dy}{dt} = 0.$

$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$

So $t_{max} = \frac{1}{K_1 - K_2} \ln \frac{k_1}{k_2}$

25. Rate constant $K = \frac{(\text{Rate})}{[\text{conc.}]} = \frac{1 \times 10^{-3}}{.1}$

$$= \frac{3 \times 10^{-3}}{.3} = 1 \times 10^{-2}\ \text{sec}^{-1}$$

26. $A \longrightarrow \text{Product}$

We know, Rate = K [conc.]^n

$1 \times 10^{-4} = K[.01]^n$ .....(i)

$1.41 \times 10^{-4} = K[.02]^n$ .....(ii)

(i) / (ii) $\Rightarrow \frac{1}{1.41} = \left(\frac{1}{2}\right)^n$

$n = \frac{1}{2}$

Then $\frac{-d(A)}{dt} = K[A]^{1/2}$

27. Rate of reaction independent of conc. of A

Net Rxn Rate $= K_1[A]^0 - K_2[B]^1$

order wrt B is 1 because rate doubles when conc. of B doubles, then Net Rxn Rate $= k_1 - k_2[B]$.

28. Equation : $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

Given, $\frac{dx}{dt} = (2 \times 10^7\ L^2\ mol^{-2}\ s^{-1})\ [Ag^+][NH_3]^2$

$$- (1 \times 10^{-2}\ s^{-1})[Ag(NH_3)_2^+]$$

For equilibrium $\frac{dx}{dt} = 0$

$2 \times 10^7 [Ag^+][NH_3]^2 - 1 \times 10^{-2} [Ag(NH_3)_2^+] = 0$

$$\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{2 \times 10^7}{1 \times 10^{-2}} = \mathbf{2 \times 10^9\ L^2\ mol^{-2}}.$$

29. Given Rxn

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\frac{dx}{dt} = 1 \times 10^2 [N_2][H_2]^3 - 1 \times 10^{-3} [NH_3]^2$

when $\frac{dx}{dt} = 0$ then $\frac{[N_2][H_2]^3}{[NH_3]^2} = 10^{-5}$

Hence the reaction will be at equilibrium at the given instant.

30. I represent kinetic but II represent equilibrium region

Because at equilibrium the concentration remains constant.

31. Rate depends only conc. of $[(CH_3)_3CCl]$ hence rate determining

Step $(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-$

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

Initial conc. 1 1

Initially

$1.0 \times 10^{-2} = K[1][1]^2$

$K = 1.0 \times 10^{-2}$

When half of reactant reacted

$$\text{Rate} = 1.0 \times 10^{-2} \left[\frac{1}{2}\right]\left[\frac{1}{2}\right]^2$$

$$\text{Rate} = 1.25 \times 10^{-3}$$

33. We know for zeroth order Rxn

For (I) $x = kt$

For (II) $t_{1/2} \propto [A_0]$ [Initial concentration]

For (III) $A_0 - \frac{A_0}{2} = k \times 100$ .....(i)

$A_0 - \frac{A_0}{4} = k \times t$ .....(ii)

$$\frac{\frac{A_0}{2}}{\left(\frac{3A_0}{4}\right)} = \frac{k \times 100}{k \times t}$$

$$t = \frac{100 \times 3}{2} = \textbf{150 minutes.}$$

34. We know $t_{av} = 1.44 \times t_{50\%}$ and $t_{75\%} = 2\, t_{50\%}$

Then $t_{50\%} < t_{av} < t_{75\%}$

35. It is properties of Ist order Rxn and other all are properties of IInd order.

36. $Na_2S_2O_3$ which react with I_2. (Iodometric titration)

37. Suppose A_t

We know $(A_0 - A_t) = kt$ for zeroth order

$(0.50 - A_t) = 0.025 \times t$

$0.50 - A_t = 0.025 \times 15$

$A_t = 0.125$ M

38. $K = \frac{2.303}{90} \log\left(\frac{100}{100-90}\right) = \frac{2.303}{90} \times \log 10$

$= \frac{2.303}{90}$ min^{-1}

$t_{1/2}$ (50% completed) $= \frac{.6932}{2.303} \times 90 = 27.08$ minutes.

39. Conc. after at 2 half life (20 minute)

$$= \left(\frac{1}{2}\right)^2 \times (\text{Initial conc.}) = \left(\frac{1}{2}\right)^2 \times 10 = 2.5\text{ M.}$$

Then Rate $= k[a_t] = \frac{.6932}{10} \times 2.5 = .06932 \times 2.5 =$ **16**

40. $^{M}_{Z}A(g) \longrightarrow {}^{M-8}_{Z-4}B(g) + (\alpha\text{ - particles})$

$$^{M}_{Z}A(g) \longrightarrow {}^{M-8}_{Z-4}B(g) + 2\,({}^{4}_{2}He\,(g))$$

1 mole	0	0
$\left(1-\frac{3}{4}\right)$	$\frac{3}{4}$	$2 \times \frac{3}{4}$

After two half life $\frac{3}{4}$ mole of A decomposes.

Total moles after 2 half life $= \left(\frac{1}{4} + \frac{3}{4} + 2 \times \frac{3}{4}\right) = 2.5$ mole

$pV = nRT$

$p \times 1 = 2.5 \times .082 \times 300$

$p = 61.5$ atm

41. There is an error of 3dps (already exist)

Then $N_0 = (23 - 3) = 20$ dps

$N_t = 10$ dps

The half life = 10 minutes

In next 10 minute $N_t = 5$ dps

Then value with error = (5 + 3) = 8 dps.

42. Saponification of ethyl acetate by NaOH is second order Rxn

Then $k = \frac{1}{t}\left[\frac{1}{a_t} - \frac{1}{a_0}\right]$

$k = \frac{1}{10}\left[\frac{1}{8} - \frac{1}{10}\right]$.

43. The rate of reaction is decided by value of rate constant which depends on energy of activation not on the value of ΔH, definitely the comparison of rate of reactions of backward reactions can be done if ΔH values are also given to us.

44. Milk turn sour at 40°C three times faster as 0°C

Then $\frac{\text{rate at } 40^\circ C}{\text{rate at } 0^\circ C} = \frac{k_{40^0C}}{k_{0^0C}}$

$$E_a = \frac{2.303\,RT_1T_2}{(T_2 - T_1)} \log\left(\frac{k_{40^0C}}{k_{0^0C}}\right)$$

$$E_a = \frac{2.303 \times 2 \times 313 \times 273 \log(3)}{40}$$

45. We know, $\log K = \log A - \dfrac{E_a}{2.303RT}$

compare this by

$y = mx + c$

$m = -\dfrac{E_a}{2.303R}$ slope of this

Given $-\dfrac{E_a}{2.303R} = -\dfrac{1}{2.303}$

$E_a = R = 2\text{ cal}$

46. Initial Rate $= k\,[A]\,[B]^2$

Rate 1 $= k\,[0.60]\,[0.80]^2$ .....(i)

Rate 2 $= k\,[A_t]\,[B_t]|^2$ .....(ii)

Given Rxn

$$\begin{array}{lllll} A(g) + & 2B(g) \longrightarrow & C(g) \;+ & D(g) & \\ 0.60\text{ atm} & 0.80\text{ atm} & 0 & 0 & t=0 \\ (0.60-0.2) & (0.80\text{–}0.40) & 0.20 & 0.20\text{ atm} & \\ 0.40\text{ atm} & 0.40\text{ atm} & 0.20\text{ atm} & 0.20\text{ atm} & t=t \end{array}$$

Put value of pressure of t = t in rate equation (II)

Rate 2 $= k\,[.40]\,[.40]^2$

$$\frac{\text{Rate}\,2}{\text{Rate}\,1} = \frac{k[.40][.40]^2}{k[.60][.80]^2} \Rightarrow \frac{\text{Rate}\,2}{\text{Rate}\,1} = \frac{2}{3} \times \frac{1}{4} = \frac{1}{6}$$

47. $\left(\dfrac{dx}{dt}\right) = k\,[H^+]^n$

Given, pH change from 2 to 1

Then H^+ concentration change from 10^{-2} M to 10^{-1} M

Then $\dfrac{\left(\dfrac{dx}{dt}\right)_1}{\left(\dfrac{dx}{dt}\right)_2} = \dfrac{k[10^{-2}]^n}{k[10^{-1}]^n}$

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{1}{100} = \left[\frac{1}{10}\right]^n,\quad n = 2$$

48. Half life period independent on conc. Hence order is unity wrt Zn

Let order with respect to H^+ ions is 'a'

Then the rate law will be Rate $= k\,[Zn][H^+]^a$

At pH = 2, $[H^+] = 10^{-2}$ So the rate law becomes

Rate $= (k[10^{-2}]^a)[Zn] = k_1\,[Zn]$

so the half life will be $T_{1/2} = \dfrac{\ln 2}{k_1} = \dfrac{\ln 2}{k(10^{-2})^a} = 10\text{ min}$

At pH = 3, $[H^+] = 10^{-3}$ So the rate law becomes

Rate $= (k[10^{-3}]^a)[Zn] = k_2\,[Zn]$

so the half life will be $T_{1/2} = \dfrac{\ln 2}{k_2} = \dfrac{\ln 2}{k(10^{-3})^a} = 100\text{ min}$

so we have $\dfrac{10}{100} = \dfrac{k(10^{-3})^a}{k(10^{-2})^a}$

which will give $10^{-1} = 10^{-a}$

Hence **a = 1**

49. In 1st order Rxn, decreases in % of concentration same in same interval of Time

$$\left[\frac{(.12-.06)}{12} \times 100\right] = 50\% \Rightarrow \frac{(.06-.03)}{.06} \times 100 = 50\%$$

so reaction must be of **first order.**

50. We know, Rate $= k\,[\text{conc.}]$

Given Rxn catalysed by HA and HB

Rate constant $k_A = k_1\,[H^+]_A$; $k_B = k_1\,[H^+]_B$

Then relative strength of acids A and B is

$$\frac{k_A}{k_B} = \frac{[H^+]_A}{[H^+]_B}$$

$$\frac{2}{1} = \frac{[H^+]_A}{[H^+]_B} = \text{strength of } \frac{[\text{Acid A}]}{[\text{Acid B}]}$$

51. Given $C = C_0\,e^{-k_1 t}$

$t_{av} = \dfrac{1}{k_1}$

Given $t = 2\,t_{av} = \dfrac{2}{k_1}$

$$\Rightarrow\; C = C_0\,e^{-k_1 \times \frac{2}{k_1}} \qquad \Rightarrow\; \frac{C}{C_0} \times 100 = \frac{100}{e^2}$$

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

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

$$\begin{array}{llll} A(g) \longrightarrow & B(g) + & C(g) & \\ 100 & 0 & 0 & t=0 \\ (100-P) & P & P & t=10\text{ min.} \end{array}$$

$100 - P + P + P = 120$

$(100 + P) = 120$

Then $k = \dfrac{2.303}{10}\log\dfrac{100}{(100-P)}$

$k = \dfrac{2.303}{10}\log\left(\dfrac{100}{80}\right)$

53. Rate constant change on changing temperature .

54. We know

$$-\frac{d(BrO_3^-)}{dt} = -\frac{1}{5}\frac{d(Br^-)}{dt} = -\frac{1}{6}\frac{d(H^+)}{dt} = +\frac{d(Br_2)}{dt}$$

Then by this relation $\frac{d(Br_2)}{dt} = -\frac{3}{5}\frac{d(Br^-)}{dt}$

55. We know

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

99.9% completion

$a = 100$

$a - x = (100 - 99.90) = .10$

Then : $t = \frac{2.303}{k}\log\left(\frac{100}{.10}\right)$

$$t = 2.303 \times 3 \times \left[\frac{1}{k}\right]$$

$$t = 6.9 \times t_{av}$$

56. Graph I – Rate independent of time, zero order Rxn.

Graph II – Half life independent of time, Ist order Rxn.

Graph III – between $\frac{1}{(a-x)}$ and time, straight line, second order Rxn.

57. According to above data.

suppose rate law, $\frac{dx}{dt} = k[CH_3COCH_3]^a[Br_2]^b[H^+]^c$

by data (i) and (ii) conc. of $[Br_2]$ increased 2 times and conc. of $[CH_3COCH_3]$ and $[H^+]$ constant rate remains same. Then zero order wrt Br_2 .

Similarly conc. of $[H^+]$ increased 2 times rate increased 2 times, so first order wrt H^+.

Similarly 1st order wrt CH_3COCH_3

Then, $\frac{dx}{dt} = k[CH_3COCH_3][H^+]$

58. Rate = k [conc]^n ⟶ Independent of conc. of A.

59. By diagram, $\Delta H^0 = y - z = x$.

60. Rate determining step is slow step

Then Rate $= k_2[SO_3 . 2H_2O]$ .....(i)

We know by fast equation

$$\frac{k_1}{k_{-1}} = \frac{[SO_3.2H_2O]}{[SO_3][H_2O]^2}$$

$$[SO_3 . 2H_2O] = \frac{k_1}{k_{-1}}[SO_3][H_2O]^2 \quad \text{....(ii)}$$

put the value of $[SO_3 . 2H_2O]$ from (ii) to (i)

$$\text{Rate} = k_2 \times \frac{k_1}{k_{-1}}[SO_3][H_2O]^2$$

$$\text{Rate} = k\,[H_2O]^2[SO_3]$$

61. $H_2O + O \longrightarrow 2OH$ $\Delta H = 72$ kg/mole

and $E_a = 77$ Kg/mole

Then we know $\Delta H = E_a - E_b$

$72 = 77 - E_b$

$E_b = 5$ KJ/mole

62. Given, $K = \frac{k_1 k_3}{k_2}$

we know that for any reaction

$$\frac{1}{k}.\frac{dk}{dT} = \frac{E_a}{RT^2}$$

so differentiating the given relation of k with k_1, k_2 & k_3 with respect to temperature, we have

$$\frac{dk}{dT} = \frac{k_2\frac{d}{dT}(k_1k_3) - k_1k_3\frac{dk_2}{dT}}{K_2^2}$$

$$= \frac{1}{k_2}\left\{k_1\frac{dk_3}{dT} + k_3\frac{dk_1}{dT}\right\} - \frac{k_1k_3k_2}{k_2^2}\frac{dk_2}{dT}$$

$$k.\frac{E_a}{RT^2} = \frac{k_1k_3}{k_2}.\frac{E_{a3}}{RT^2} + \frac{k_3k_1}{k_2}.\frac{E_{a1}}{RT^2} - \frac{k_1k_3}{k_2}.\frac{E_{a2}}{RT^2}$$

$E_a = Ea_3 + Ea_1 - Ea_2$

$= (20 + 40 - 30) =$ **30 kJ/mol**

64. More is the activation energy less is the rate of reaction.

65. Rate = K $[A]^n [B]^m$

Given, doubling the concentration of A and halving the concentration of B

then $\text{Rate}_2 = K[2A]^n \left[\frac{B}{2}\right]^m$

$\text{Rate}_2 = K[A]^n [B]^m \times 2^{(n-m)}$

67.

$$2A + B \longrightarrow C$$

t = 0   2a   a   0

t = t   2a – 2x   a – x   x

$$\frac{d[C]}{dt} = k\,(2\,(a-x)\,(a-x)^{-1}) = 2k \Rightarrow \int d[c] = \int k\,dt$$

$\Rightarrow$ [C] = 2 kt

unit of k = Ms^{-1}

[A] = 2 (a – x) and [C] = x

[B] = (a – x).

70.

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

t = 0   400   0   0

t = 20 min   400 – p   2p   p

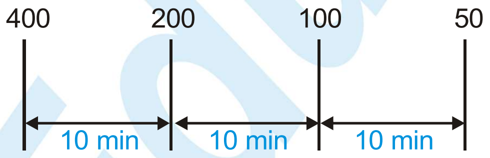
Given   400 – p + 2p + p = 1000

400 + 2p = 1000

$$p = 300\text{ mm}; k = \frac{1}{20}\ln\frac{400}{400-300} = \frac{1}{20}\ln 4$$

$$\Rightarrow k = \frac{\ln 2}{10}\text{ min}^{-1}$$

$T_{1/2}$ = 10 min ;   Value of K = 0.0693 min^{-1}



After 30 min Partial Pressure of A is 50 mm, After 30 min Partial Pressure of B is 700 mm

After 30 min Partial Pressure of C is 350 mm , After 30 min total pressure become 1100 mm

71. For figure-1 :

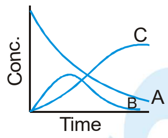


Figure 1

the rate of formation of B is higher than rate of formation of C. Hence $K_1 >> K_2$.

For figure-2 :

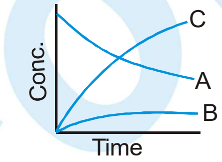


Figure 2

the rate of formation of C is greater than rate of formation of B. Hence $K_2 >> K_1$.

72. By using maxwell's velocity distribution curve the rise in temperature, increases the activated molecules to form the product therefore rate of reaction increases.

Part # II : Assertion & Reason

1. According to arrhenius equation $K = Ae^{-Ea/RT}$ when E_a = 0, K = A

5. Number of half lives = $n = \frac{t}{T} = \frac{200}{100} = 2$

$$\therefore \frac{N}{N_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^2 = \frac{1}{4} = \frac{1}{4}\times 100\% = 25\%.$$ The assertion is not true.

EXERCISE - 3

Part # I : Matrix Match Type

1.

(A) r = k [A] [B]

i.e. II^{nd} order reaction

unit of k = mol^{-1} lt $time^{-1}$

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

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

$(t_{1/2})_A = (t_{1/2})_B$ if A and B are taken in stoichiometric ratio.

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

$r = k_2[B]^o[A] = k_2[A]$

unit of k = time^{-1} does not have concentration unit.

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2[A]$$

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

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

$r = k_3[A]^o[B]^o$

unit of k = mole litre^{-1} time^{-1}

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_3$$

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

(D) $2A + B \longrightarrow 2C + 3D$

$r = K_3[A]^o[B]^o$

unit of K = mol lt^{-1} time^{-1}

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[C]}{dt} \Rightarrow -\frac{d[A]}{dt} = \frac{d[C]}{dt}$$

3. **(A)** $2.303 \log_{10}\frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_2T_1}\right] \Rightarrow \frac{K_2}{K_1} = 11$

$T_2 = 298\,K;\ T_1 = 273\,K,\ E_a = 65000\,J,\ R = 8.314\ J/(mol\,K)$

(B) $\frac{2.5}{20} = \frac{1}{8} = \left(\frac{1}{2}\right)^n \Rightarrow n = 3 \Rightarrow t = 3 \times \frac{0.693}{0.0693} = 30$

(C) Zero order : $t_{1/2} = \frac{a}{2K}$ I order : $t_{1/2} = \frac{0.693}{K}$

$$\frac{1}{2K_1} = \frac{0.693}{K_2} \Rightarrow \frac{K_2}{K_1} = 2 \times 0.693$$

(D) $t_{1/2} \propto (a)^{1-n}$ or $(1-n) = \frac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''}$

$$t_{1/2} \propto \frac{1}{a^{n-1}} \Rightarrow \frac{480}{240} = \left(\frac{0.0677}{0.136}\right)^{n-1} \quad n = 0$$

Part # II : Comprehension

Comprehension : 2

(1 to 3)

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

$$P_C = \frac{1}{3}[P_0 + P_C]$$

$$3P_C = P_0 + P_C$$

$$2P_C = P_0$$

$$P_C = \frac{P_0}{2}$$

$$P_T = P_0 - p + 2p + P_C + p = P_0 + P_C + 2p$$

$$P_\infty = 2P_0 + P_0 + P_C \qquad = 3P_0 + P_C$$

$$P_T = \frac{1}{2}P_\infty \text{ (given)}$$

$$P_0 + P_C + 2p = \frac{1}{2}[3P_0 + P_C]$$

$$\frac{3P_0}{2} + 2p = \frac{1}{2}\left[3P_0 + \frac{P_0}{2}\right]$$

$$\frac{3P_0}{2} + 2p = \frac{1}{2} \times \frac{1}{2} \times 7P_0$$

$$2p = \frac{7}{4}P_0 - \frac{3P_0}{2}$$

$$2p = \frac{P_0}{4}$$

$$\mathbf{P = \frac{P_0}{8}}$$

$$P_\infty = 3P_0 + P_C = 35$$

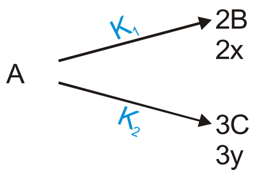
$$= 3P_0 + \frac{P_0}{2} = 35$$

$$= \frac{7P_0}{2} = 35$$

$$\mathbf{P_0 = 10\ bar}$$

Comprehension : 3

1.



t = 0 a

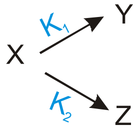
t − t a − x − y

$$\therefore\ [A]_0 = [A]_t + \frac{[B]_t}{2} + \frac{[C]_t}{3}$$

$$a = a - x - y + \frac{2x}{2} + \frac{3y}{3}$$

a = a

2.



$$\frac{[X]_t}{[Y]_t + [Z]_t} =$$

$$\frac{ae^{-(k_1+k_2)t}}{\frac{k_1a}{k_1+k_2}[1-e^{-(k_1+k_2)t}] + \frac{k_2a}{(k_1+k_2)}[1-e^{-(k_1+k_2)t}]}$$

$$= \frac{ae^{-(k_1+k_2)t}}{[1-e^{-(k_1+k_2)t}]\left[\frac{k_1a+k_2a}{k_1+k_2}\right]}$$

$$= \frac{e^{-(k_1+k_2)t}}{1-e^{-(k_1+k_2)t}}$$

$$= \frac{1}{[e^{(k_1+k_2)t}-1]} = \frac{1}{[e^{kt}-1]} \quad [\text{where } k = k_1 + k_2]$$

4. $\frac{[B]_t}{[C]_t} = \frac{3k_1}{4k_2}$ which depends only on temperature not on time.

Comprehension : 4

Sol. (1 to 3)

1. **(I)** Rate law for mechanism I

Rate = $k_1^{\,1}[A][B] \Rightarrow$ Rate = $1 \times 10^{-5}[0.1][0.1]$

= 1×10^{-7} m/sec .

2. **(II)** Rate = $1 \times 10^{-4} \times [1] = 1 \times 10^{-4}$

3. **(III)** Rate I = Rate II

$$k_1^{\,1}[A][B] = k_1[A] \quad \Rightarrow \quad B = \frac{k_1}{k_1^1} = 10\ \text{M}$$

Comprehension : 5

Sol. (1 to 3)

1. (I) Rate = $\frac{dc}{dt} = \left(\frac{\Delta c}{\Delta t}\right) = \frac{.0033}{25} = 1.32 \times 10^{-4}$

(II) Rate = $\frac{dc}{dt} = \left(\frac{\Delta c}{\Delta t}\right) = \frac{.0039}{15} = 2.6 \times 10^{-4}$

(III) Rate = $\left(\frac{\Delta c}{\Delta t}\right) = \frac{.0077}{15} = 1.02 \times 10^{-3}$

2. (II) Rate of Rxn = Rate of formation of C.

Then we say by I data.

Suppose $[\text{Rate} = k[A]^a[B]^b]$ ....(i)

$1.32 \times 10^{-4} = k[.10]^a[.05]^b$ ....(ii)

$2.6 \times 10^{-4} = k[.10]^a[.10]^b$ ....(iii)

$1.02 \times 10^{-3} = k[.20]^a[.10]^b$ ....(iv)

By equation (ii) and (iii) we find b = 1

By (iii) and (iv) we find a = 2.97 ≈ 3.

Then Rate = $k[A]^2[B]^1$

3. (III) Rate $1.32 \times 10^{-4} = k[.10]^2[.05]$

$k = 2.6 \times 10^{-1}$

Comprehension : 6

1. (C) $-\frac{1}{a}\frac{d[A]}{dt} = \frac{1}{b}\frac{d[B]}{dt}$

or $-\frac{d[A]}{dt} = \frac{a}{b}\frac{d[B]}{dt}$

or $\log\left[-\frac{d[A]}{dt}\right] = \log\frac{a}{b} + \log\frac{d[B]}{dt}$

$\therefore\ \log\frac{a}{b} = 0.3 \qquad \therefore\ \frac{a}{b} = 2$

2. (A) E_a is always positive thus K increases with temperature.

ΔH is –ve, $\frac{K_f}{K_b}$ decreases with temperature.

ΔH is +ve, $\frac{K_f}{K_b}$ increases with temperature.

3. **(D)** Rate or reaction $= -\frac{d[A]}{dt} = +\frac{d[B]}{dt} = +\frac{1}{2}\frac{d[C]}{dt}$

Also rate of reaction,

$$-\frac{d[A]}{dt} = K\,[A]^1 = 10^{-2} \times \frac{5}{2}$$

$$= 2.5 \times 10^{-2}\ \text{mol L}^{-1}\,\text{t}^{-1}$$

$\because$ P = C R T

$$\therefore\ -\frac{d[A]}{dt} = -\frac{1}{RT}.\frac{d[P]}{dt}$$

$$\therefore\ -\frac{d[P_A]}{dt} = RT\frac{d[A]}{dt} = 0.0821 \times 300 \times 2.5 \times 10^{-2}$$

$$= 6.15 \times 10^{-1}\ \text{atm t}^{-1}$$

$$\frac{d[C]}{dt} = 2\left[-\frac{d[A]}{dt}\right]$$

$$= 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2}\ \text{mole L}^{-1}\text{t}^{-1}$$

4. **(A)** Rate $= -\frac{dC_A}{dt} = K\,C^a{}_A$

$$\therefore\ \log\left[-\frac{dC_A}{dt}\right] = \log K + a\log C_A$$

$\therefore$ log K = 0.6

K = 3.98 time^{-1} and a = 1 = tanθ (θ = 45°).

Comprehension : 7

Sol. (1 to 4)

1. **(A)** According to the given condition reaction is Ist order with respect to N_2O_5.

2. **(B)** $2N_2O_5 \longrightarrow 4\,NO_2 + O_2$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{d\,[N_2O_5]}{dt} = \frac{1}{4}\frac{d\,[NO_2]}{dt}$$

$$= \frac{d\,[O_2]}{dt} = K\,[N_2O_5]^n$$

$$-\frac{d\,[N_2O_5]}{dt} = K_1\,[N_2O_5]^n = 2K\,[N_2O_5]^n$$

$$\frac{d\,[NO_2]}{dt} = K_2\,[N_2O_5]^n = 4K\,[N_2O_5]^n$$

$$\frac{d\,[O_2]}{dt} = K_3\,[N_2O_5]^n = K\,[N_2O_5]^n$$

$K_1 = 2K,\ K_2 = 4K,\ K_3 = K$

3. **(B)** $\frac{d\,[O_2]}{dt} = 16\ \text{g/hr} = \frac{16}{32}\ \text{mol hr}^{-1} = \frac{1}{2}\ \text{mol hr}^{-1}$

$$\frac{d\,[NO_2]}{dt} = \frac{4d\,[O_2]}{dt} = 4 \text{ x } \frac{16}{32} = 2\ \text{mol hr}^{-1}$$

$$= 2 \text{ x } 46 = 92\ \text{g hr}^{-1}$$

$$\frac{-d[N_2O_5]}{dt} = \frac{2d\,[O_2]}{dt} = 2 \text{ x } \frac{16}{32} = 1\ \text{mol hr}^{-1}\ 1 \text{ x } 108$$

$$= 108\ \text{g hr}^{-1}$$

4. **(C)**

	N_2O_5	$\longrightarrow$	$2NO_2 +$	$\frac{1}{2}O_2$
Initial mole	4		0	0
moles after diss	0		8	2

$$\therefore\ \text{Mole ratio} = \frac{4}{10} = 2.5$$

$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{6.2\times10^{-4}} = 1117.7$ sec but it depends upon temperature as K also depends upon temperature.

$$t_{40\%} = \frac{2.303}{6.2\times10^{-4}}\log\frac{100}{60} = 822.98\ \text{sec}$$

Rate = $K[N_2O_5]$; Thus $r_1 = K\,[N_2O_5]$

If V is doubled the concentration becomes half

$$\therefore\ r_2 = K\,\frac{1}{2}[N_2O_5] \quad \Rightarrow \quad \therefore\ \frac{r_1}{r_2} = \frac{2}{1}$$

EXERCISE - 4

Subjective Type

2. $CH_3COOC_2H_5 + NaOH_{(aq)} \longrightarrow CH_3COONa + C_2H_5OH$

t = 0	a	b
t = t	(a–x)	(b–x)
t = ∞	0	(b–a)

$$\text{At time t} = 0\quad \frac{b\times100}{1000} = \frac{0.05\times75}{1000}$$

$$\text{so b} = \frac{0.05\times75}{100} \quad \Rightarrow \quad b = \frac{0.15}{4}$$

$$\text{At time t} = 30\ \text{min}\quad \frac{(b-x)\times50}{1000} = \frac{0.05\times25}{1000}$$

$$(b-x) = \frac{0.05}{2}$$

$$x = \left(b - \frac{0.05}{2}\right) = \frac{0.15}{4} - \frac{0.05}{2} = \frac{0.15 - 0.1}{4} = \frac{0.05}{4}$$

At time $t = \infty$ $\quad \frac{(b-a)\times 25}{1000} = \frac{0.05 \times 6.25}{1000}$

$$(b–a) = \frac{0.05}{4}$$

$$a = b - \frac{0.05}{4} = \frac{0.15}{4} - \frac{0.05}{4} = \frac{0.1}{4}$$

$$K = \frac{1}{t(b-a)} \ln \left(\frac{a\,(b-x)}{b\,(a-x)}\right)$$

$$K = \frac{1 \times 4}{30 \times 0.05} \ln \left(\frac{\frac{0.1}{4} \times \frac{0.05}{2}}{\frac{0.15}{4} \times \frac{0.05}{4}}\right)$$

$$K = \frac{4}{30 \times 0.05} \ln \left(\frac{0.1 \times 2}{0.15}\right) = \frac{4}{1.5}\,[2\ln 2 – \ln 3]$$

Ans. $\quad k = 0.736$ litre/mol/minute

3. $\quad B^{n+} \longrightarrow B^{(n+4)+}$

millimole at $t = 0 \quad a \qquad 0$

$$2e + B^{n+} \longrightarrow B^{(n-2)+}$$

$t = t \qquad (a - x) \qquad x$

$$5e + B^{(n+4)+} \longrightarrow B^{(n-1)+}$$

Let normality be N for reducing agent.

Thus, at $t = 0$ $a \times 2 = N \times 25$

$\therefore \quad a = \frac{25}{2} N$

at $t = t \quad (a - x) \times 2 \; + \; x.5 \; = \; N \times 32$

$\therefore \quad 3x = 7N$

or $\quad x = \frac{7}{3} N$

Now, $\quad K = \frac{2.303}{10} \log \frac{\frac{25}{2} N}{\left(\frac{25}{2} - \frac{7}{3}\right) N} = \frac{2.303}{10} \log \frac{25 \times 6}{2 \times 61}$

$= 2.07 \times 10^{-2}\ \text{min}^{-1}$

4. $\quad 2\,NH_3 \longrightarrow N_2 + 3H_2$

$$r = k\,[NH_3]^0 = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = +\frac{1}{3}\frac{d[H_2]}{dt}$$

$$= 2.5 \times 10^{-4} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = 2.5 \times 10^{-4}$$

$$\frac{d[H_2]}{dt} = 7.5 \times 10^{-4}$$

(d) $\quad \frac{-d[NH_3]}{dt} = \frac{k_1[NH_3]}{1 + k_2[NH_3]}$

(i) NH_3 is very – very Less $\quad \frac{-d[NH_3]}{dt} = k_1[NH_3]$

$\longrightarrow$ First order

(ii) NH_3 is very – very High $\quad \frac{-d[NH_3]}{dt} = \left(\frac{k_1}{k_2}\right)$

$\longrightarrow$ zero order

6. The Rate equation $\frac{-d[A]}{dt} = k\,[A]^a\,[H^+]^b$

During any experiment pH is constant

$$\frac{-d[A]}{dt} = k'\,[A]^a \quad \text{where } k' = k\,[H^+]^b$$

Since Half is independent of the Initial conc. of A

Hence $a = 1$

First order w.r.t A. $\qquad$ Now k′ is First order rate

$$\text{constant}k^1 = \frac{0.693}{t_{1/2}}$$

$$\frac{(T_{50})_1}{(T_{50})_2} = \frac{k'_2}{k'_1} = \frac{k[H^+]_2^b}{k[H^+]_1^b} = \frac{[H^+]_2^b}{[H^+]_1^b} \Rightarrow \left(\frac{100}{10}\right)$$

$$= \left(\frac{10^{-4}}{10^{-5}}\right)^b \quad \Rightarrow \quad b = 1$$

So $\quad \frac{-d[A]}{dt} = k\,[A]\,[H^+]^1$

8. ● – potassium chromo - oxalate $\rightleftharpoons$ d potassium chromo oxalate

$t=0$	a	0
$t=t_{eq.}$	$(a-x_{eq.})$	$x_{eq.}$

$$K_{eq.}=\frac{K_f}{K_b}=\left(\frac{x_{eq.}}{a-x_{eq.}}\right)$$

As $x_{eq.}=\frac{a}{2}$; $K_f=K_b$

$$(K_f+K_b)=\frac{2.303}{t}\log\left(\frac{x_{eq.}}{x_{eq.}-x}\right)$$

$$2K_f=\frac{2.303}{560}\log\left(\frac{0.5a}{0.5a-0.12a}\right)$$

$$2K_f=5.42\times10^{-4}$$

$$K_f=K_b=2.71\times10^{-4}$$

11.

	$A \longrightarrow$	Product
$t=0$	a	0
$t=60$ min	$0.8a$	
$t=90$min	$0.40a$	
$t=100$ min	$0.10a$	

In absence of catalyst

$$K=\frac{2.303}{60}\log\frac{a}{0.8a}=\frac{2.303}{60}\log\left(\frac{5}{4}\right) \qquad \text{....(i)}$$

For Ist catalyst

$$(K_{cat.})_{Ist}=\frac{2.303}{30}\log\left(\frac{0.8a}{0.40a}\right)=\frac{2.303}{30}\log 2.$$

$$\frac{(K_{cat.})_{I^{st}}}{K}=\frac{\frac{2.303}{30}\log 2}{\left(\frac{2.303}{60}\right)\times\log\left(\frac{5}{4}\right)}=\frac{2\log 2}{\log 5-\log 4}=\frac{2\times0.30}{0.1}$$

$$\frac{(K_{cat.})_{I^{st}}}{K}=6.21$$

$$\frac{(K_{cat.})_{I^{st}}}{K}=e^{\left(\frac{E_a-E_a^1}{RT}\right)}$$

$$6.21=e^{\left(\frac{E_a-E_a^1}{RT}\right)}$$

$$2.303\log 6.21=\frac{80-E_a^1}{RT}$$

$$E_a=80-\frac{2.303\times0.793\times8.314\times300}{1000}=\mathbf{80-4.56=75.44\ kJ.}$$

12. $$\frac{d[N_2O_5]}{dt}=-K_a[N_2O_5]+K_a'[NO_2][NO_3] \qquad \text{.....(1)}$$

$$\frac{d[NO_3]}{dt}=K_a[N_2O_5]-K_a'[NO_2][NO_3]-K_b[NO_2][NO_3]$$

$$-K_c[NO][NO_3]=0$$

$$K_a(N_2O_5)=K_a'[NO_2][NO_3]+K_b[NO_2][NO_3]$$

$$+K_c[NO][NO_3] \qquad \text{......(2)}$$

$$\frac{d[NO]}{dt}=+K_b[NO_2]-K_c[NO]$$

$$[NO]=\frac{K_b[NO_2]}{K_c} \qquad \text{......(3)}$$

$$K_a(N_2O_5)=K_a'[NO_2][NO_3]+K_b[NO_2][NO_3]+K_b[NO_2][NO_3]$$

$$K_a(N_2O_5)=K_a'[NO_2][NO_3]+2K_b[NO_2][NO_3]$$

$$[NO_3]=\frac{K_a[N_2O_5]}{K_a'[NO_2]+2K_b[NO_2]}$$

$$\frac{d[N_2O_5]}{dt}=-K_a[N_2O_5]+\frac{K_a'[NO_2]\times K_a[N_2O_5]}{K_a'[NO_2]+2K_b[NO_2]}$$

$$\frac{d[N_2O_5]}{dt}=-K_a[N_2O_5]+\frac{K_a'\times K_a[N_2O_5]}{K_a'+2K_b}$$

$$\frac{d[N_2O_5]}{dt}=-\frac{K_aK_a'[N_2O_5]-2K_aK_b[N_2O_5]+K_aK_a'[N_2O_5]}{[K_a'+2K_b]}$$

$$\frac{d[N_2O_5]}{dt}=-\frac{-2K_aK_b[N_2O_5]}{K_a'+2K_b}$$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt}=\left(\frac{K_aK_b[N_2O_5]}{K_a'+2K_b}\right)$$

13.

		A $\rightleftharpoons$	B	
t=0		100	0	
t=1 hr		$(100-x_1)$	x_1	$(x_1=30)$
t=4 hr		$(100-x_2)$	x_2	$x_2=?$
t=∞	At eq.	$100-70$	70	so $x_{eq.}=70$

$$K=\frac{1}{1}\ln\left(\frac{70}{70-X_1}\right)=\frac{1}{4}\ln\left(\frac{70}{70-x_2}\right)$$

$$=\ln\left(\frac{70}{70-25}\right)=\frac{1}{4}\ln\left(\frac{70}{70-x_2}\right)$$

$$=\ln\left(\frac{70}{45}\right)^4=\ln\left(\frac{70}{70-x_2}\right)$$

$x_2=58\%$

so % of A remaining $=42\%$.

15. (i) A $\longrightarrow$ Product (ii) B $\longrightarrow$ Product

For I^st reaction

$$\left(\frac{K_{310}}{K_{300}}\right)_A=2.$$

$$\text{At } 310\text{ K } \frac{\ln 2}{(K_{310})_A}$$

$(K_{310})_A=0.0231.$

$(K_{310})_B=2\,(K_{310})_A=0.0462.$

For A $$\log\left(\frac{K_{310}}{K_{300}}\right)_A=\frac{E_A}{2.303R}\left[\frac{310-300}{310\times 300}\right]$$

For B $$\log\left(\frac{K_{310}}{K_{300}}\right)_B=\frac{E_B}{2.303R}\left[\frac{310-300}{310\times 300}\right]$$

$$\frac{\log\left(\frac{K_{310}}{300}\right)_A}{\log\left(\frac{K_{310}}{K_{300}}\right)_B}=\left(\frac{E_A}{E_B}\right)\Rightarrow\frac{0.3}{\log\left(\frac{K_{310}}{K_{300}}\right)_B}=2$$

$$0.3=2\log\left(\frac{K_{310}}{K_{300}}\right)_B\Rightarrow\left(\frac{K_{310}}{K_{300}}\right)_B=1.421$$

$$(K_{300})_B=\frac{K_{310}}{1.421}=\frac{0.0462}{1.421}=0.0327\text{ min}^{-1}.$$

16. $$\frac{d[HBr]}{dt}=K_2[H_2][Br]+K_3[H][Br_2]-K_4[H][HBr]$$

$$\frac{d[HBr]}{dt}=K_2[H_2][Br]+K_3[H][Br_2]-K_4[HBr][H]$$

Now, $$Br_2\underset{K_5}{\overset{K_1}{\rightleftharpoons}}2Br$$

$$\frac{K_1}{K_5}=\frac{[Br]^2}{[Br_2]}$$

so $$[Br]=\left(\frac{K_1}{K_5}\right)^{1/2}[Br_2]^{1/2}\qquad\text{.....(1)}$$

At steady state,

$$\frac{d[H]}{dt}=K_2[Br][H_2]-K_3[H][Br_2]-K_4[H][HBr]=0$$

So, $$[H]=\frac{K_2[H][Br]}{K_3[Br_2]+K_4[HBr]}$$

$$\frac{d[HBr]}{dt}=K_2[H_2][Br]+\Big[K_3[Br_2]-K_4[HBr]\Big]\frac{K_2[H_2][Br]}{K_3[Br_2]+K_4[HBr]}$$

$$\frac{d[HBr]}{dt}=K_2[H_2][Br]\left[1+\frac{K_3[Br_2]-K_4[HBr]}{K_3[Br_2]+K_4[HBr]}\right]$$

$$\frac{d[HBr]}{dt}=K_2\left(\frac{K_1}{K_5}\right)^{1/2}[H_2][Br_2]^{1/2}\left[\frac{K_3[Br_2]+K_4[HBr]+K_3[Br_2]-K_4[HBr]}{K_3[Br_2]+K_4[HBr]}\right]$$

$$\frac{d[HBr]}{dt}=K_2\left(\frac{K_1}{K_5}\right)^{1/2}[H_2][Br_2]^{1/2}\left[\frac{2K_3[Br_2]}{K_3[Br_2]+K_4[HBr]}\right]$$

$$\frac{d[HBr]}{dt}=2K_2\left(\frac{K_1}{K_5}\right)^{1/2}[H_2][Br_2]^{1/2}\left[\frac{1}{1+\frac{K_4}{K_3}\frac{[HBr]}{[Br_2]}}\right]$$

So, $$\frac{d[HBr]}{dt}=\frac{2K_2\left(\frac{K_1}{K_5}\right)^{1/2}[H_2][Br_2]^{1/2}}{1+\frac{K_4}{K_3}\frac{[HBr]}{[Br_2]}}$$

18. → $k = Ae^{-E_a/RT}$

case I. $k_1 = Ae^{-100/RT}$

case II. $k_2 = Ae^{-25/RT}$

$$\therefore \quad \frac{k_1}{k_2} = \frac{e^{-100/RT}}{e^{-25/RT}} e^{-75/RT}$$

$$\text{or} \quad \log_e \frac{k_2}{k_1} = \log\ e^{+75/RT} \qquad (\Delta H \text{ in kJ})$$

$$\log_e \frac{k_2}{k_1} = \frac{75}{RT} = \frac{75\times10^3}{8.314\times293} \qquad (\Delta H \text{ in kJ})$$

$$\frac{K_2}{K_1} = 2.35 \times 10^3$$

Since, $r = k\,[A]^n$ → n and [A] are same for case I and II.

$$\therefore \quad \frac{r_2}{r_1} = \frac{k_2}{k_1} = \mathbf{2.35 \times 1013}$$

19. $\lambda_A = \lambda_1 + \lambda_2 = 1.5 \times 10^{-5} + 5 \times 10^{-6}$

$= 20 \times 10^{-6}\ \text{sec}^{-1}$

$$[C]_t = \frac{2\lambda_2}{\lambda_1+\lambda_2}\,[A]_0\,[1 - e^{-(K_1+K_2)t}] = \frac{2\times5\times10^{-6}}{20\times10^{-6}} \times 0.25$$

$[1 - e^{-(20\times10^{-6}\times5\times3600)}] = 3.7 \times 10^{-2}$ M.

20. For A : $\text{rate} = k_A\,[A]^1$ .... (i)

$$\text{and } (t_{1/2})_A = \frac{0.693}{k_A} \qquad \text{... (ii)}$$

For B : $\text{rate} = k_B\,[B]^2$ ... (iii)

$$\text{and } (t_{1/2})_B = \frac{1}{a.k_B} \qquad \text{... (iv)}$$

where a is initial concentration.

(a) Initial rate of A, $r_A = k_A \times a$

Initial rate of B, $r_B = k_B \times a^2$

$$\therefore \quad \frac{r_A}{r_B} = \frac{k_A}{k_B} \times \frac{1}{a} \qquad \text{... (v)}$$

From Eq. (ii) and (iv) if $(t_{1/2})_A = (t_{1/2})_B$, then $\dfrac{0.693}{k_A} = \dfrac{1}{k_B.a}$

$$\text{or} \quad \frac{k_A}{k_B} = 0.693 \times a \qquad \text{... (vi)}$$

$$\therefore \quad \text{From Eqs. (v) and (vi), } \frac{r_A}{r_B} = \frac{0.693a}{a} = \mathbf{0.693}$$

(b) After lapse of I half, the new rates are r^t_A and r^t_B

$$r^t_A = k_A \times \frac{a}{2}\ ;\ r^t_B = k_B \times \left(\frac{a}{2}\right)^2$$

$$\therefore \quad \frac{r^t_A}{r^t_B} = \frac{k_A}{k_B} \times \frac{2}{a} \qquad \text{... (vii)}$$

$$\text{By Eqs. (vi) and (vii)} \quad \frac{r^t_A}{r^t_B} = 0.693 \times a \times \frac{2}{a} = \mathbf{1.386}$$

21.

	A	$\longrightarrow$	nB
t = 0	A_0		0
t = t	$A_0(1-X)$		$nA_0.X$

At intersection point O obtained after time t,

[A] = [B]

$$\therefore \quad A_0(1-X) = nA_0.X$$

$$\therefore \quad X = \frac{1}{1+n}$$

$$\therefore \quad [B] = \frac{nA_0}{1+n}$$

22. (i) Rate of forward reaction $= 2.0 \times 10^{-4}\,[Cu(NH_3)_4]^{2+}$
Rate of backward reaction $= 3.0 \times 10^5$
$[Cu(NH_3)_3\,H_2O]^{2+}\,[NH_3]$
(ii) Therefore, $k_f = 2.0 \times 10^{-4}$ & $k_b = 3.0 \times 10^5$

$$\therefore \quad \frac{k_f}{k_b} = \frac{2.0\times10^{-4}}{3.0\times10^{-5}} = \mathbf{6.6 \times 10–19\ litre\ mol–1}$$

equilibrium constant is very less therefore backward reaction is predominant.

23. For reaction (a) : $K_1 = A_1e^{-Ea_1/Rt}$ or 2.79×10^{-3}

$$= A_1\,e^{-\frac{12\times10^3}{RT}} \qquad \text{... (i)}$$

For reaction (b) : $K_2 = A_2e^{-Ea_2/Rt}$ or 1.52×10^{-4}

$$= A_2\,e^{-\frac{24.5\times10^3}{RT}} \qquad \text{... (ii)}$$

By Eq. (i) $$A_1 = \frac{2.79\times10^{-3}}{\exp\left(-\frac{12\times10^3}{2\times510}\right)} = \frac{2.79\times10^{-3}}{7.8\times10^{-6}}$$

$$= 3.5\times10^2$$

By Eq. (ii) $$A_2 = \frac{1.52\times10^{-4}}{\exp\left(-\frac{24.5\times10^3}{2\times510}\right)} = \frac{1.52\times10^{-4}}{3.7\times10^{-11}}$$

$$= 4.1\times10^6$$

If rate constants of two reaction are same, the reactions will give equimolar mixture of products. Let these are same at temperature T, i.e.,

$$A_1e^{-Ea_1/Rt} = A_2e^{-Ea_2/Rt}$$

$$3.5\times10^2\times e^{-\frac{12\times10^3}{RT}} = 4.1\times10^6\times e^{-\frac{24.5\times10^3}{RT}}$$

or $$e^{\frac{10^3}{RT}[24.5-12.0]} = \frac{A_2}{A_1} = \frac{4.10\times10^6}{3.5\times10^2} = \mathbf{1.17\times10^4}$$

or $$\frac{10^3}{RT}\times12.5 = 9.37$$

∴ $$T = \frac{12.5\times10^3}{9.37\times2} = 667\text{ K}$$

∴ $T = \mathbf{394^\circ\ C}$

24. Given, $A \rightleftharpoons nB$

$$\text{Loss in concentration of A in 1 hour} = \frac{0.6-0.5}{1} = 0.1$$

$$\text{Gain in concentration of B in 1 hour} = \frac{0.2-0}{1} = 0.2$$

(i) ✈ 0.1 mole of A gives to 0.2 moles of B in a given time and thus,

$n = 2$

(ii) ✈ Equilibrium is attained after 5 hrs. where [B] = 0.6 and [A] = 0.3

$$\text{Equilibrium constant, } K = \frac{[B]^2}{[A]} = \frac{[0.6]^2}{0.3}$$

= **1.2 mole litre–1**

(iii) Initial rate of conversion of A = changes in conc. of A during 1 hour $= \frac{0.1}{1} =$ **0.1 mole litre–1 hour–1**

25.

$$\begin{array}{llll} & A & + \quad OH^- & \longrightarrow \text{Products} \\ t=0 & 0.002 & \quad 0.3 & \\ t=30 & \left[0.002-\frac{0.002\times1}{100}\right] & \left[0.3-\frac{0.002\times1}{100}\right] & \end{array}$$

For II order reaction having $[A] \neq [OH^-]$

$$k\times t = \frac{2.303}{[A]_0-[OH^-]_0}\log\frac{[OH^-]_0[A]_t}{[A]_0[OH^-]_t}$$

Using, $$k = \frac{2.303}{30\times(0.002-0.3)}\log\frac{0.3\times\left[0.002-\frac{0.002\times1}{100}\right]}{0.002\times\left[0.3-\frac{0.002\times1}{100}\right]}$$

k = 1.12 × 10–3 litre mol–1 sec–1

26. ✈ $$k = \frac{2.303}{t} = \log\frac{a}{(a-x)}$$

Hint : Use hit and trial method.

Case I : $a \propto 200$ mm ;

$x \propto 200\times(50/100)$ mm and $t_{1/2} = 53$ minute

∴ $$k_1 = \frac{2.303}{53}\log\frac{200}{200-100}$$

$= 1.307\times10^{-2}\text{ minute}^{-1}$

Case II : $a \propto 200$ mm ;

$x \propto 200\times(73/100)$ mm $\propto 146$ mm

and $t_{73\%} = 100$ minute

∴ $$k_2 = \frac{2.303}{100}\log\frac{200}{200-146}$$

$= 1.309\times10^{-2}\text{ minute}^{-1}$

(a) Since, the value of k is constant for the given data using I order reaction and thus reaction is of **I order**.

(b) $$k = \frac{k_1+k_2}{2} = \frac{(1.309+1.307)\times10^{-2}}{2} = \mathbf{1.308\times10^{-2}}$$

(c) For a Ist order reaction $t_{(1/n)} \propto (a)^0$ and therefore if initial pressure is 600 mm, the decomposition in 100 minute will be **73%.**

27. $CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$

Pressure at $t = 0$ 0.40

Pressure at $t = 12$ min

$(0.40 - P)$ P P P

For ideal gas behaviour moles ∝ pressure

$\therefore$ $a \propto 0.40,\ (a - X) \propto (0.40 - P)$

✈ $$K = \frac{2.303}{t}\log\frac{a}{(a - X)}$$

or $$\frac{0.693}{14.5} = \frac{2.303}{12}\log\frac{0.40}{(0.40 - P)}$$

$\therefore$ $P = 0.175$ atm

Thus, total pressure after 12 minutes $= 0.40 - P + P + P + P$

$= 0.40 + 2P$

$= 0.40 + 2 \times 0.175 =$ **0.75 atm**

28. $$t = \frac{2.303}{K}\log\frac{a}{(a - X)}$$

If $t = t_{1/2},\quad X = \frac{a}{2}$;

$$\therefore\quad t_{1/2} = \frac{2.303}{K}\log\frac{a}{a - (a/2)} \quad \text{... (i)}$$

If $t = t_{99\%},\quad X = \frac{99a}{100}$;

$$t_{99\%} = \frac{2.303}{K}\log\frac{a}{a - (99a/100)} \quad \text{... (ii)}$$

By Eqs. (i) and (ii), $t_{99\%} = \frac{\log 100}{\log 2} \times t_{1/2} = \frac{2}{0.3010} \times 2.1$

= **13.95 hour**

Also, Moles of N_2O formed $= (99/100) \times$ moles of NH_2NO_2 taken

$$= \frac{99}{100} \times \frac{6.2}{62} = 0.099$$

$\therefore$ Volume of N_2O formed at STP $= 0.099 \times 22.4$

= **2.2117 litre**

29. Let rate $= K\,[CH_3COF]^a\,[H_2O]^b$

It is given that in case I : $[H_2O] >> [CH_3COF]$

and in case II : $[H_2O] << [CH_3COF]$

Thus, according to ostwald isolation method, we can assume $[H_2O]$ in excess in case I and $[CH_3COF]$ in excess case II.

Thus, for case I :

Using I order for CH_3COF, we have

$$K_t = 2.303\log\frac{a}{(a - X)}$$

$$\therefore\quad K_t = \frac{2.303}{10}\log\frac{0.01}{0.00857} = 0.0154\ \text{min}^{-1}$$

and $$K_2 = \frac{2.303}{10}\log\frac{0.01}{0.00735} = 0.0154\ \text{min}^{-1}$$

Thus, $K_{av} = 0.0154\ \text{min}^{-1}$

Thus, order with respect to $[CH_3COF]$ is one or $a = 1$

Similarly, for case II :

Using I order for H_2O, we have

$$K_t = 2.303\log\frac{a}{(a - X)}$$

$$K'_1 = \frac{2.303}{10}\log\frac{0.02}{0.00176} = 0.0128$$

$$K'_2 = \frac{2.303}{20}\log\frac{0.02}{0.00156} = 0.0124$$

$$K'_3 = \frac{2.303}{40}\log\frac{0.02}{0.00122} = 0.0124$$

(almost constant, i.e. $K'_{av} = 0.0125\ \text{min}^{-1}$)

Thus, order with respect to $[H_2O]$ is one or $b = 1$

Now rate $= K_T = [CH_3COF]^1\,[H_2O]^1$

Also rate $= K\,[CH_3COF]^1\,[H_2O]^0$ case I

$$\therefore\quad \frac{K_T}{k} = [H_2O]^1$$

or $K_T = K \times [H_2O]^1$

$= 0.0154 \times 1.0 =$ **1.54 × 10–2 min–1**

30. For 99% completion, $$t_{90\%} = \frac{2.303}{k} \times \log\frac{100}{100 - 99} \quad \text{... (i)}$$

For 90% completion, $$t_{90\%} = \frac{2.303}{k} \times \log\frac{100}{100 - 90} \quad \text{... (ii)}$$

By Eqs. (i) and (ii) $$\frac{t_{99\%}}{t_{99\%}} = \frac{\log 100}{\log 10} = 2$$

$\therefore$ $t_{99\%} = 2 \times t_{90\%}$

31. To provide a long time or heating to a reaction mixture means that reaction has gone to completion.

	$A \longrightarrow$	B +	$2C$
Moles before dissociation	a	0	0
Moles after dissociation	$(a-X)$	X	$2X$
Moles after complete diss.	0	a	$2a$

✈ Total moles at a time $\propto$ pressure at that time

$a \propto P_0 \qquad t = 0 \qquad$ ... (i)

$\therefore \quad a + 2X \propto 264 \qquad t = 14$ minute $\qquad$ ... (ii)

$3a \propto 264 \qquad t = \propto \qquad$ ... (iii)

(a) $\therefore$ By Eqs. (i) and (ii) $\quad P^o = $ **150 mm**

(b) ✈ By Eqs. (ii) and (iii) $X \propto 57$

$$K = \frac{2.303}{14}\log\frac{150}{150-57} = \textbf{3.415 × 10–2 min–1}$$

(c) $$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{3.415\times10^{-2}} = \textbf{20.29 min}$$

32. $\qquad A \longrightarrow B$

$x_0 \qquad y_0$

$(x_0 - a) \qquad (y_0 + a)$

$= x \qquad = y$

$\therefore \quad x + y = x_0 - a + y_0 + a = x_0 + y_0$

$$-\frac{dx}{dt} = Kx.y$$

Put $x_0 - a = x$

$$\therefore \quad -\frac{da}{dt} = \frac{dx}{dt}$$

$$\frac{da}{dt} = K\,(x_0 - a)\,(y_0 + a)$$

$= K\,[x_0\,y_0 + ax_0 - ax_0 - a^2]$

$= K\,[x_0\,y_0 + (x_0 - y_0)\,a - a^2]$

$$= K\left[(x_0y_0) - \left\{a^2 - 2\left(\frac{x_0-y_0}{2}\right).a - \left(\frac{x_0-y_0}{2}\right)^2 + \left(\frac{x_0-y_0}{2}\right)^2\right\}\right]$$

$$= K\left[x_0y_0 - \left(a - \frac{x_0-y_0}{2}\right)^2 + \left(\frac{x_0-y_0}{2}\right)^2\right]$$

$$= K\left[\left(\frac{x_0+y_0}{2}\right)^2 - \left(a - \left(\frac{x_0-y_0}{2}\right)\right)^2\right]$$

On integrating,

$$Kt + C = \frac{1}{\frac{2(x_0+y_0)}{2}}\log\frac{\frac{x_0+y_0}{2} + \left[a - \frac{x_0-y_0}{2}\right]}{\frac{x_0+y_0}{2} - \left[a - \frac{x_0-y_0}{2}\right]}$$

$$Kt + C\ \frac{1}{x_0+y_0}\log\frac{a+y_0}{(x_0-a)}$$

at $\quad t = 0, \qquad a = 0$

$$C = \frac{1}{x_0+y_0}\log\frac{y_0}{x_0}$$

$$\therefore \quad Kt = \frac{1}{x_0+y_0}\log\frac{a+y_0}{(x_0-a)}.\frac{x_0}{y_0} = \frac{1}{x_0+y_0}\log\frac{y.x_0}{x.y_0}$$

$$= \frac{2.303}{(x_0+y_0)}\log\frac{y.x_0}{x.y_0}$$

33. $$\log_{10}K = \frac{3163}{T} + 12$$

at T (T ij) $= (273 + 43.3) = 316.3$ K

$$\log_{10}K = \frac{3163}{316.3} + 12$$

$\log_{10}K = (10+12) = 22$

$K = 10^{22}$

Then half life period

$$t_{1/2} = \left(\frac{1}{K\times a}\right) = \frac{1}{10^{22}\times.001} = \frac{1}{10^{19}} = 10^{-19}$$

$t_{1/2} = 10^{-19}$ min $\qquad$ **Ans.** $\qquad 10^{-19}$ minute.

34. Decomposition of H_2O_2 Ist order (Rxn)

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

Then we know

$$K = Ae\,\frac{-Ea}{RT}$$

For uncatalysed Rxn

$$K_1 = Ae\,\frac{-Ea}{RT} \qquad [T = 300\,K, R = 2]$$

$$K_1 = Ae\,\frac{-18\times10^3}{2\times300} \qquad ....(i)$$

and for catalysed Rxn

$$K_2 = Ae\,\frac{-6\times10^3}{2\times300} \qquad ....(ii)$$

Equation (ii) / (i)

$$\frac{K_2}{K_1} = e\frac{(18-6)\times 10^3}{2\times 300}$$

$$\frac{K_2}{K_1} = e^{20}$$

$$\frac{K_2}{K_1} = 4.85\times 10^8$$

Then catalysed reaction is 4.85×10^8 times faster than uncatalysed Rxn.

35. We know, Rate = K [conc]^n for nth order Rxn.

Then, $$\frac{Rate_2}{Rate_1} = \left(\frac{conc_2}{conc_1}\right)^n$$

given, $Rate_2 = Rate_1$, $conc_2 = (conc_1 \times 1.5)$

$2.25 = (1.5)^n$

n = 2 second order Rxn

36. (a) Rxn zero order w.r.t. to A then.

when half of A reacted

$$\begin{array}{lcccc} & A & + B & + C & \longrightarrow \text{Product} \\ \text{at } t=0 & a_0 & a_0 & a_0 & \\ \text{at } t=1000 \text{ sec.} & \frac{a_0}{2} & \frac{a_0}{2} & \frac{a_0}{2} & \end{array}$$

Then we know for zero orders Rxn $(a_0 - a_t) = kt$

given $a_t = \frac{a_0}{2}$.

Then $$k \times t = \frac{a_0}{2}$$

$$k = \frac{a_0}{2\times t} = \frac{a_0}{2\times 1000} = \frac{a_0}{2000}$$

at t= 2000 sec.

$$a_0 - a_t = \frac{a_0}{2000}\times 2000$$

$a_t = 0$ zero fraction left.

(b) IInd order w.r.t. A then similarly 50% completed

$$k = \frac{1}{1000}\left[\frac{1}{\left(\frac{a_0}{2}\right)} - \frac{1}{a_0}\right]$$

$$k = \frac{1}{1000}\times\left(\frac{1}{a_0}\right)$$

Then after 2000 sec.

$$k = \frac{1}{2000}\left[\frac{1}{a_t} - \frac{1}{a_0}\right]$$

$$\frac{1}{1000}\times\frac{1}{a_0} = \frac{1}{2000}\left[\frac{1}{a_t} - \frac{1}{a_0}\right]$$

$$\left[\frac{2}{a_0} + \frac{1}{a_0}\right] = \frac{1}{a_t}$$

$$\frac{3}{a_0} = \frac{1}{a_t}$$

$$a_t = \frac{a_0}{3}$$

Fraction left $\frac{a_t}{a_0} = \frac{1}{3}$

37. $CH_3COCH_3(g) \longrightarrow C_2H_6(g) + CO(g)$

$t = 0$ .5

$t = t$ .4

Then by given data

$$\frac{.6932}{81} = \frac{2.303}{t}\log\left(\frac{0.5}{0.4}\right)$$

$$t = \frac{2.303\times 81}{.6932}\times\log(1.25)$$

$t = 26.07$ sec

38. For $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

$x \propto V_t$,

$a \propto V_\infty$

$a - x \propto (V_\infty - V_t)$

Then for Ist order Rxn

$$0.008 = \frac{2.303}{20}\log\frac{V_\infty}{(V_\infty - V_t)}$$

$$0.008 = \frac{2.303}{20}\log\frac{V_\infty}{(V_\infty - 16)}$$

$$\frac{0.008\times 20}{2.303} = \log\frac{V_\infty}{(V_\infty - 16)}$$

$$0.06947 = \log\frac{V_\infty}{(V_\infty - 16)}$$

Then, $V_\infty = 108.23$ mL

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

We know for first order Rxn

$$k = \frac{2.303}{t} \log\left(\frac{P_0}{P_t}\right)$$

P_0 = Initial pressure of A

P_t = Pressure A after time t.

$$\begin{array}{lccccl} A & \longrightarrow B\ + & C & + & D & \\ P_0 & 0 & 0 & & 0 & \text{at } t=0 \\ [P_t = (P_0 - x)] & x & x & & x & \text{at } t=t \end{array}$$

Given $(P_0 - x + x + x + x) = P$

$$(P_0 + 2x) = P$$

$$x = \frac{(P - P_0)}{2}$$

Then $(P_0 - x) = \left(P_0 - \frac{(P-P_0)}{2}\right) = \frac{(3P_0 - P)}{2}$

40. We know for IInd order Rxn.

$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$ (because concentration of both reactants are equal)

when Rxn completed 20% $= (a-x) = \frac{80}{100} \times [a]$

Then $k = \frac{1}{500}\left[\frac{1}{\frac{80a}{100}} - \frac{1}{a}\right] \Rightarrow k = \frac{1}{500}\left[\frac{100}{80a} - \frac{1}{a}\right]$

$$k = \frac{1}{500 \times a}\left[\frac{100}{80} - 1\right]$$

$$\Rightarrow \frac{1}{500} \times \frac{20}{80} \times \frac{1}{a} = \frac{1}{500 \times 4} \times \frac{1}{a} = \frac{1}{2000a}$$

$$k = \frac{1}{2000a}$$

For 60% completed

$$(a-x) = \left(a - \frac{60}{100}a\right) = \frac{40a}{100}$$

Then $k = \frac{1}{t}\left[\frac{1}{\frac{40a}{100}} - \frac{1}{a}\right]$

$$\Rightarrow \frac{1}{2000a} = \frac{1}{a \times t}\left[\frac{100}{40} - 1\right]$$

$$\Rightarrow \frac{1}{2000} = \frac{1}{t}\left[\frac{60}{40}\right] \Rightarrow t = 3000 \text{ sec}$$

41. Suppose order of Rxn is n

Then $t_{1/2} \propto \left(\frac{1}{P_0}\right)^n$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{(P_o)_2}{(P_0)_1}\right)^n$$

From (i) and (ii) data.

$$\left(\frac{3.52}{1.82}\right) = \left(\frac{100}{50}\right)^{n-1}$$

$$1.934 = (2)^{(n-1)}$$

$$(1.9569) = (2)^{(n-1)}$$

$n = 2$ IInd order Rxn.

42. Containing mixture of compound A and B both decomposed with first order kinetics

$t_{1/2}$ for $A = 54$ min $t_{1/2}$ for $B = 18$ min

Given :

$A_t - A_o\, e^{-k_1 t}$ .... (i)

$B_t - B_o\, e^{-k_2 t}$ .... (ii)

$A_o = B_o$

$A_t - 4B_t$

by (i)/(ii)

$$\frac{4B_t}{B_t} = \left(\frac{B_o e^{-k_1 t}}{B_o e^{-k_2 t}}\right)$$

$$4 = e^{(k_2 - k_1)t}$$

$$\ln 4 = (k_2 - k_1)\, t$$

$$t = \frac{\ln 4}{(k_2 - k_1)} = \frac{\ln 4}{(k_2 - k_1)} = \frac{\ln 4}{\frac{0.6932}{18} - \frac{0.6932}{54}} = \textbf{53 min.}$$

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

Second order W.R.T.A

Then $t_{1/2} = \dfrac{1}{ka_0}$

$$t_{1/2} = \frac{1}{0.622 \times 4.10 \times 10^{-2}} = \mathbf{39.2\ min.}$$

44. $CH_3COCH_2COOH \xrightarrow[1^{st}\ OR]{H^+} CO_2 + CH_3COCH_3$

45. **(i)** $r = K[O][O_2]$

$0.15 = 1.5 \times 10^7 [O][O_2]$

$0.15 = 1.5 \times 10^7 \times 4.08 \times 10^{-5} \times [O].$

$[O] = 2.45 \text{ x } 10^{-4}.$

(ii) $\dfrac{d[O_2]}{dt} = 2r = 0.15 \times 2 = 0.3.$

46.

$CH_3OCH_3(g)$	$\longrightarrow$	$CH_4(g)$	+ $CO(g)$	+ $H_2(g)$
$P_0 = 4mm$		0	0	0
$P_t = (P_0 - x)$		x	x	x

we known

$P_t = p_0 e^{-Kt}$

$\dfrac{P_t}{p_0} = e^{-Kt}$

$\dfrac{P_t}{p_0} = e^{-(4.78 \text{ x } 10^{-3} \text{ x } 4.5 \text{ x } 60)}$

$\dfrac{P_t}{p_0} = e^{-1.29} = 0.275$

Sine composition is same therefore

$\dfrac{r_2}{r_1} = \dfrac{P_2}{P_1} = 0.275$ **Ans. 0.275**

47. $Rate = k[B][A]$

$Rate = k'[A]$

$k' = k[B]$

$= 5 \times 10^{-3} \times 6$

$= 3 \times 10^{-2}$

$(C_t)_A = C_0 e^{-kt}$

$= 0.1\ e^{-3 \times 10^{-2} \times 100}$

$= 0.1\ e^{-3} = 0.005$ min

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. The concentration of the reactant decreases from 0.8 M to 0.4 M in 15 minutes, i.e., $t_{1/2} = 15$ minute. Therefore, the concentration of reactant will fall from 0.1 M to 0.025 in two half live. i.e., $2t_{1/2} = 2 \times 15 = 30$ minutes.

2. $2A + B \longrightarrow C$ $rate = k[A][B]$

The value of k (velocity constant) is always independent of the concentration of reactant and it is a function of temperature only.

3. $t_{1/2} = 4$ hours $n = \dfrac{T}{t_{1/2}} = \dfrac{24}{4} = 6;$ $N = N_0\left(\dfrac{1}{2}\right)^N$

or, $N = 200 \times$

$$\left(\frac{1}{2}\right)^6 = 200 \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = 3.125g.$$

4. For endothermic reaction, $\Delta H =$ ve

$\Delta H = E_f - E_b$, it means $E_b < E_f$.

5. Generally, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation. Thus, a reaction involving two different reactants can never be unimolecular.

6. Given $rate = k[CO]^2$

Thus, according to the rate law expression doubling the concentration of CO increases the rate by a factor of 4.

7. $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$

$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$ [rate determining step]

Rate of the reaction $(r) = k[NOBr_2][NO]$

where $[NOBr_2] = K_c[NO][Br_2]$

$r = k.K_C.[NO][Br_2][NO]$

$r = k'[NO]^2[Br_2].$

The order of the reaction with respect to $NO(g) = 2$.

8. $\Delta H_R = E_f - E_b = 180 - 200 = -20\ kJ\ mol^{-1}$

The correct answer for this question should be $-20kJ\ mol^{-1}$. But no option given is correct. Hence we can ignore sign and select option

9. Let A be the activity for safe working.

Given $A_o = 10A$ $Ao \times No$ and $A \times N$

$$t = \frac{2.303}{\lambda}\log\frac{N_o}{N} = \frac{2.303}{\lambda}\log\frac{A_o}{A}$$

$$= \frac{2.303}{\frac{0.693}{30}}\log\frac{10A}{A} = \frac{2.303\times 30}{0.693}\log 10 = \frac{2.303\times 30}{0.693}$$

$= 99.69$ days ≈ 100 days.

10. $\frac{1}{2}A \longrightarrow 2B$

$$-\frac{1}{1/2}\frac{d(A)}{dt} = \frac{1}{2}\frac{d(B)}{dt}$$

$$\boxed{-\frac{d(A)}{dt} = \frac{1}{4}\frac{d(B)}{dt}}$$

11. In first order reaction for X% completion

$$k = \frac{2.303}{t}\log\left(\frac{100}{100 - x\%}\right)$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\left(\frac{100}{100-99}\right)$$

$$= \frac{0.693}{6.93} = \frac{2.303\times 2}{t}$$

So, $t = 46.06$ min.

12. $A \longrightarrow$ product

For zero order reaction

$t_{1/2} \propto \frac{1}{a^{n-1}}$ a = initial concentration of reactant

$t_{1/2} \propto a$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_1}{a_2}\ ; \quad \frac{1}{(t_{1/2})_2} = \frac{2}{0.50}$$

$$t_{1/2} = \frac{0.5}{2} = 0.25\ \text{h.}$$

13. Mechanism (1) rate $= K[Cl_2][H_2S]$

Mechanism (2) rate $= K_1[Cl_2][HS^-]$

$$K_{eq} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$[HS^-] = \frac{K_{eq}[H_2S]}{[H^+]}$$

$$= K_1K_{eq}\frac{[Cl_2][H_2S]}{[H^+]}$$

$\therefore$ Mechanism (1) is consistent with this rate equation.

14. $$\frac{\text{Rate at } 50^\circ C}{\text{Rate at } T_1\,^\circ C} = (2)^{\frac{\Delta T}{T_1}} = (2)^{\frac{50}{10}} = 2^5$$

$= 32$ times

15. $K_1 = A_1e^{-Ea_1/RT}$

$K_2 = A_2e^{-Ea_2/RT}$

$$\frac{K_1}{K_2} = \frac{A_1}{A_2}e^{(E_{a_2}-E_{a_1})/RT}$$

$$K_1 = K_2A \times e^{E_{a_1}/RT}$$

16. $$K = \frac{1}{40}\ln\frac{0.1}{0.025} = \frac{1}{40}\ln 4$$

$R = K[A]^1$

$$= \frac{1}{40}\ln 4(.01) = \frac{2\ln 2}{40}(.01) \quad = \mathbf{3.47 \times 10^{-4}}$$

17. $$\log\frac{K_2}{K_1} = \frac{-E_a}{2.030R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\frac{K_2}{K_1} = 2$; $T_2 = 310$ K $\quad T_1 = 300$ K

$$\Rightarrow \log 2 = \frac{-E_a}{2.303\times 8.134}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$\Rightarrow E_a = 53598.6$ J / mol $= 53.6$ KJ/mol

Ans is (1)

18. $$k = \frac{1}{50}\ln\left(\frac{0.500}{0.125}\right) = \frac{1}{50}.\ln(4) = \frac{2\ln(2)}{50}$$

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

$$\text{POR} = \frac{d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{1}{1/2}\frac{d[O_2]}{dt}$$

$$\frac{2}{50}\ln(2)\times 0.05 = 2.\frac{d[O_2]}{dt}$$

$$\frac{d[O_2]}{dt} = 0.693\times 10^{-3} = 0.93\times 10^{-4}\ \text{mol/min}$$

19. From arrhenius equation

$$K = A.e^{\frac{-Ea}{RT}}$$

so, $K_1 = A.e^{-E_{a_1}/RT}$ .... (1)

$K_2 = A.e^{-E_{a_2}/RT}$ .... (2)

so, equation (2)/(1) $\Rightarrow \frac{K_2}{K_1} = e^{\frac{(E_{a_1} - E_{a_2})}{RT}}$

(As pre-exponential factors of both reactions is same)

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{E_{a_1} - E_{a_2}}{RT} = \frac{10,000}{8.314 \times 300} = 4$$

20. $CH_3CHO \longrightarrow CH_4 + CO$

$r_1 = 1$ torr sec^{-1}, when 5% reacted (95% unreacted)

$r_2 = 0.5$ torr sec^{-1}, when 33% reacted (67% unreacted)

$r \propto (a-x)^m$ m = order of reaction

$a - x$ = unreacted

$$\frac{r_1}{r_2} = \left[\frac{(a-x_1)}{(a-x_2)}\right]^m \Rightarrow \frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)^m$$

$$2 = (1.41)^m \Rightarrow 2 = \left(\sqrt{2}\right)^m \Rightarrow m = 2$$

Part # II : IIT-JEE ADVANCED

1. Since 0.01 M of X changes to 0.0025 M in 40 minutes, $t_{1/2}$ of reaction = 40/2 = 20 minutes Rate of reaction of

$$r = k[X] = \frac{0.693}{t_{1/2}} \times [X] = \frac{0.693}{20} \times 0.01$$

$= 3.47 \times 10^{-4}$ M min^{-1}.

2. **(a)** From the rate law expression, $R_0 = k[A_0]^a[B_0]^b$ and from the table it is clear that :

(i) when the concentration of $[A_0]$ is doubled, keeping $[B_0]$ constant (see readings 1 and 2), the rate also doubles i.e. rate is directly proportional to $[A_0]$ or a = 1.

(ii) when the concentration of $[B_0]$ is reduced, keeping $[A_0]$ constant (see readings 1 and 3), the rate remains constant i.e., rate is independent of $[B_0]$ or b = 0. Thus, rate equation becomes $R_0 = k[A_0]$.

(b) $k = \frac{R_0}{[A_0]} = \frac{0.05}{0.10} = 0.5$ sec^{-1}.

3.

$$\begin{array}{lllll} & 2X(g) & \longrightarrow 3Y(g) & + 2Z(g) & \\ t = 0 & 800 & - & - & \\ t & 800 - 2x & 3x & 2x & = (800 + 3x) \end{array}$$

from given data in time 100 min the partial pressure of X decreases from 800 to 400 so $t_{1/2}$ 100 min. Also in next 100 min Px decreases from 400 to 200 to again $t_{1/2} = 100$ min. Since half left is independent of initial concentration so reaction must Ist order with respect to X.

Rate constant $K = \frac{\ln 2}{t_{1/2}} = 6.93 \times 10^{-3}$ min^{-1}.

Time taken for 75% completion = 2 × $t_{1/2}$ = 200 min.

Now when Px = 700 = 800 – 2x so x = 50 mm of Hg

so total pressure = 800 + 3x = 950 mm of Hg

4. Rate of exchange of ^{14}C between atmosphere and living organism is so fast that an equilibrium is set up between the intake of ^{14}C by organism and its exponential decay.

5. Fossil has 6000 year age for the determination of the age of old organism.

6. $\lambda = \frac{1}{T_1 - T_2} \ln \frac{C_1}{C_2}$.

7. $aG + bH \longrightarrow$ products

Rate = $k[G]^x[H]^y$

$R = K[G]_0^x[H]_0^y$ (Let initial conc. are $[G]_0$ & $[H]_0$)

$8R = K[2G]_0^x[2H]_0^y = K2^x.2^yR$

so $2^{x+y} = 8 \Rightarrow x + y = 3$

8. For Ist order reaction

For zero order reaction

$$k_1 = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{40} \text{ second}^{-1}$$

$$k_0 = \frac{C_0}{2\,t_{1/2}} = \frac{1.386}{2 \text{ x } 20} \Rightarrow \frac{k_1}{k_0} = \frac{0.693}{1.386} = 0.5.$$

9. From Arrhenius equation

$K = Ae^{-Ea/RT}$

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

$$2.303 \log K = 2.303 \log A - \frac{Ea}{RT}$$

$$\log K = \frac{-Ea}{2.303R} \times \frac{1}{T} + \log A \qquad \text{....... (A)}$$

$$\log K = -(2000)\frac{1}{T} + 6 \qquad \text{........(B)}$$

On comparing equation (A) and (B)

$$\frac{-Ea}{2.303R} = -2000.$$

$Ea = 2.303 \times 8.314 \times 2000 = 38.29$ kJ and $\log A = 6$

$A = 10^6$

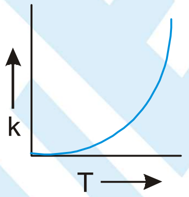
10. $$K = \frac{C_0 - C}{t} = \frac{1-0.75}{0.05} = \frac{0.25}{0.05} = 5$$

$$K = \frac{0.75-0.40}{0.07} = \frac{0.35}{0.07} = 5$$

So, reaction must be of zero order.

11. $k = Ae^{-Ea/RT}$

So, variation will be



12.* $C_t = C_0 e^{-Kt}$

$t_{1/2} \propto \frac{1}{K}$, K ↑ on increasing T.

After eight half lives,

$$C = \frac{C_o}{2^8}$$

$$\Rightarrow \% \text{ completion} = \frac{C_o - \frac{C_o}{2^8}}{C_0} \times 100 = 99.6\%$$

13. $$Kt_{1/8} = \text{In}\left\{\frac{C_O}{C_O/8}\right\} = \text{In } 8$$

$$Kt_{1/10} = \text{In}\left\{\frac{C_O}{C_O/10}\right\} = \text{In } 10$$

then $$\frac{t_{1/8}}{t_{1/10}} \times 10 = \frac{\text{In } 8}{\text{In } 10} \times 10 = \frac{\log 2}{\log 10} \times 10 = 9$$

14. For P, if $t_{50\%} = x$

then $t_{75\%} = 2x$

This happens only in first order reaction.

so, order with respect to P is 1.

For Q, the graph shows that concentration of Q decreases linearly with time. So rate, with respect to Q, remains constant. Hence, it is zero order wrt Q.

So, overall order is 0 + 1 = 1 → Ans. is D

15. A high activation energy usually implies a slow reaction.

16. $$\text{Steric factor(P)} = \frac{(A/Z)\text{exp}}{(A/Z)\text{theo}}$$

A = frea.factor

Z = Collision freq.

usually P < 1

$\therefore A_{exp} < A_{theo}$. Assuming 'Z' to be same

Here P > 1

$\therefore \quad A_{exp} > A_{theo}$

17. $$A(g) \xrightarrow{\text{First order}} 2B(g) + C(g) \quad V = \text{constant},$$

T = 300 K

$t = 0 \quad P_0$

$t = t_{1/3} \quad \left(P_0 - \frac{2P_0}{3}\right) \quad \frac{4P_0}{3} \quad \frac{2P_0}{3}$

$= \frac{P_0}{3}$

$t = t \quad P_0 - x \quad 2x \quad x$

So, $P_t = P_0 - x + 2x + x = P_0 + 2x$

or $2x = P_t - P_0$

$$t = \frac{1}{k}\ln\frac{P_0}{(P_0 - x)}$$

or $$t = \frac{1}{k}\ln\frac{P_0}{P_0 - \frac{(P_t - P_0)}{2}} = \frac{1}{k}\ln\frac{2P_0}{2P_0 - P_t + P_0}$$

or $$Kt = \ln\frac{2P_0}{3P_0 - P_t}, \; Kt = \ln 2P_0 - \ln(3P_0 - P_t)$$

or $\ln(3P_0 - P_t) = -Kt + \ln 2P_0$

Graph between $\ln(3P_0 - P_t)$ vs 't' is a straight line with negative slope.

So (A) is correct option.

$t_{1/3} = \frac{1}{K}\ln\frac{P_0}{(P_0/3)} = \frac{1}{K}\ln 3 \Rightarrow$ It is independent of initial concentration.

So (B) is wrong option.

As rate constant is a constant quantity and independent of initial concentration.

So Graph (D) is correct.

18. $A(g) + B(g) \rightleftharpoons AB(g)$

$E_{a_b} = E_{a_f} + 2RT$ & $A_f = 4\,A_b$

Now, Rate constant of forward reaction $k_f = A_f e^{-Ea_f/RT}$

Rate constant of reverse reaction $K_b = A_b e^{-E_{ab}/RT}$

Equilibrium constant

$$K_{eq} = \frac{K_f}{K_b} = \frac{A_f}{A_b}e^{-(E_{af} - E_{ab})/RT}$$

$$= 4e^{+2} = 4e^2$$

Now, $\Delta G° = -RT\ln K_{eq} = -2500\ln(4e^2)$

$= -2500(\ln 4 + \ln e^2)$

$= -2500(1.4 + 2) = -2500 \times 3.4$

$= -8500$ J/mole

MOCK TEST

1. **(C)**

2. **(C)**

3. **(C)**

As only A is optically active. So conc. of A at t = 20 min $\propto 30°$

While concentration of A at t = 50 min $\propto 15°$

So conc. has decreased to half of its value in 30 min, so $t_{1/2} = 30$ min.

So volume consumed of H_2O_2 at t = 30 min = $t_{1/2}$, is according to 50% production of B.

at t = 90 min. production of B = 87.5% (Three half lives)

$$\text{So volume consumed} = (30\text{ ml}) + \left(\frac{30}{2}\text{ml}\right) + \left(\frac{30}{4}\right)\text{ ml}$$

= 52.5 ml ans.

4. **(B)**

$r_2 = k_2[A]_2^{\ 1}[B]_2^{\ 1}$ for a certain run

$r_1 = k_1[A]_1^{\ 1}[B]_1^{\ 1}$ for a previous run

dividing, we get

$$\frac{r_2}{r_1} = \frac{k_2}{k_1}\,\frac{[A]_2}{[A]_1}\,\frac{[B]_2}{[B]_1}$$

Substituting the given information

$$1.5 = 2^{\left(\frac{t_2-27}{10}\right)} \times \frac{1}{2} \times \frac{1}{2}$$

$$\Rightarrow \quad 6 = 2^{\left(\frac{t_2-27}{10}\right)} \quad \Rightarrow \quad \frac{t_2-27}{10} \bullet n2 = \bullet n6$$

$$\Rightarrow \quad \frac{t_2-27}{10} = \frac{1\,n\,6}{1\,n\,2} \quad \Rightarrow \quad t_2 = 52.85°C \approx 53°C$$

5. **(C)**

$$\frac{[B]}{[C]} = \frac{3k_1}{8k_1} = \frac{3}{8} = \alpha$$

$$\frac{[C]}{[D]} = \frac{8k_2}{7.5k_2} = \frac{8}{7.5} = \beta$$

$\therefore \quad \alpha\beta = 0.4$

6. **(C)**

$t_{1/2} = Ka^{(1-n)}$, n being order = Rate constant

$\log t_{1/2} = \log K + (1 - n)\log a$

$1 - n = -\quad 1$

$n = 2$

7. **(D)**

Rate $(SN^2) = 5.0 \times 10^{-5} \times 10^{-2}[R-X] = 5.0 \times 10^{-7}[R-X]$

Rate $(SN^1) = 0.20 \times 10^{-5}[R-X]$

$$\%\text{ of } SN^2 = \frac{5\times10-7[R-X]\times100}{5\times10^{-7}[R-X]+0.20\times10^{-5}[R-X]} = 20$$

8. **(D)**

$$\frac{k_t}{k_0} = (TC)^{t-0/10}$$

$$\text{Taking log gives } \log_e k_t - \log_e k_0 = \frac{t}{10}\log_e(TC)$$

$$\Rightarrow \quad \ln kt = \ln k_0 + \left(\frac{\ln(TC)}{10}\right)t$$

$$\text{Comparision indicates } \frac{\ln(TC)}{10} = \frac{\ln 3}{10}$$

$$\Rightarrow \qquad TC = 3$$

9. **(C)**

$k = -2.303\text{ (slope) min}^{-1} = -2.303\,(-0.03)\text{ min}^{-1} = 0.06909\text{ min}^{-1} = 4.14\text{ hr}^{-1} \approx 4\text{ hr}^{-1}$

10. **(A)**

$$\frac{n_{CH_4} + n_{CO_2}}{n_{CH_2CO} + n_{H_2O}} = \frac{k_1}{k_2}$$

$$\Rightarrow \quad \frac{n_{CH_4} + n_{CO_2}}{n_{CH_4} + n_{CO_2} + n_{CH_2CO} + n_{H_2O}} = \frac{k_1}{k_1 + k_2}$$

$$\Rightarrow \quad \frac{2n_{CH_4}}{n_{total}} = \frac{k_1}{(k_1 + k_2)}$$

$$\Rightarrow \quad \frac{n_{CH_4}}{n_{total}} = \frac{k_1}{2(k_1 + k_2)}$$

$$\Rightarrow \quad \frac{n_{CH_4}}{n_{total}} \times 100 = \frac{50k_1}{(k_1 + k_2)}$$

11. (B)

At pH = 5 the $t_{1/2} \propto [\text{sugar}]^0$ or the reaction is first order w.r.t. sugar because $t_{1/2}$ remains same for any conc. of sugar.

so rate = $k\,[\text{sugar}]^1\,[H^+]^n$

[n = order w.r.t. H^+ ion]

Also $t_{1/2}$ for $[H^+] \propto \dfrac{1}{[C_0]^{n-1}}$ or $\propto C_0^{\,1-n}$

$\therefore\quad 600 \propto [10^{-5}]^{1-n}$

$60 \propto [10^{-6}]^{1-n}$

or $\quad 10 = (10)^{1-n}$ $\quad$ or $\quad 1 - n = 1$

$n = 0$

12. (C)

Rate is governed by slowest step

$$A + B_2 \xrightarrow{k_1} AB + B$$

$$r = k1\,[A]\,[B_2] \qquad \text{......(i)}$$

From $A_2 \overset{k_c}{\rightleftharpoons} A + A$

$$k_C = \frac{[A]^2}{[A_2]} \qquad \text{......(ii)}$$

$$[A] = \sqrt{k_C}\;[A_2]^{1/2}$$

$$r = k_1\sqrt{k_C}\;[A_2]^{1/2}\,[B_2] \qquad \text{order is} = \frac{1}{2} + 1 = \frac{3}{2}$$

13. (A)

14. (B)

rate is slope of curve

at 20 sec $\dfrac{y_2 - y_1}{x_2 - x_1} = \dfrac{0.35}{50}$ (approx)

$= 7 \times 10^{-3}$ M sec^{-1}

at 40 sec rate become half because of first order

$r_{40\text{sec}} = 3.5 \times 10^{-3}$ M sec^{-1}

$r_{60\text{sec}} = 1.75 \times 10^{-3}$ M sec^{-1}

$$r_{80\text{sec}} = \frac{1.75}{2} - 10^{-3}$$

$$A \longrightarrow B$$

t = 0 0.4

t = 60 $\quad 0.4 - x \quad x$

$= 0.05 \quad 50\ x = 0.35$

15. (B C)

16. (A B D)

17. (A B D)

0	30	x
30	20	– 15

$$k = \frac{1}{30}\,2.3\log\frac{45}{35}$$

$\therefore\quad t_{1/2} = 75$ min

$$k = \frac{1}{t}\,2.3\log\frac{45}{0-(-15)}$$

t = 120 min

$$\frac{30-(-15)}{x-(-15)} = 2 \text{ at half time}$$

$$\Rightarrow \frac{45}{x+15} = 2 \qquad \Rightarrow \qquad x + 15 = \frac{45}{2}$$

$\Rightarrow\quad x = 22.5 - 15 = 7.5°$

18. (A, B, C, D)

19. (AB)

$$r_B = \frac{dC_B}{dt} = \frac{1}{V}\frac{dn_B}{dt} = \frac{1}{V}\frac{d(C_B V)}{dt}$$

$$= \frac{V}{V}\frac{dC_B}{dt} + \frac{C_B}{V}\frac{dV}{dt} = \frac{dC_B}{dt} + \frac{C_B}{V}\frac{dV}{dt}$$

20. (D)

According to arrhenius equation $K = Ae^{-Ea/RT}$ when $E_a = 0,\ K = A$.

21. (C)

22. (B)

It is fact

23. (B)

$$\log K_b = \log A - \frac{Ea}{2.303RT}$$

$$\log K_b = 12 - \frac{57450}{2.303 \times 8.314 \times 300}$$

$\text{Log}\ K_b = 2$

$K_b = \text{Antilog}\ 2$

$K_b = 10^2$

$$K_c = \frac{K_F}{K_b} \Rightarrow 10^4 = \frac{K_F}{10^2} \qquad \Rightarrow \qquad K_F = 10^6$$

24. (A)

$\Delta G = \Delta H - T\Delta S$

$\Delta G = 20 - T \times 0.07$

For non-spontaneous process $\Delta G > 0$

hence $0 < 20 - T \times 0.07$

$$T < \frac{20}{0.07} \Rightarrow T < 285.7\ \text{K}$$

25. (C)

$K_p = K_c(RT)^{\Delta n}$

$= 10^4(0.082 \times 300)^1$

$= 24.6 \times 10^4$

26. (A)

$$-\frac{dA}{dt} = k_f[A] - k_b[C]$$

and $\dfrac{d[C]}{dt} = k_f[A] - k_b[C]$ at any time

and slope between conce and time is known as rate and they are always equal at any time.

27. (D)

28. (D)

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C$$

$$K_C = \frac{k_f}{k_b} = \frac{[C]}{[A]} = \frac{0.4}{0.6} = \frac{2}{3} \text{ from graph}$$

2 C f 2A

$$K'_C = \left(\frac{1}{K_C}\right)^2 = \left(\frac{3}{2}\right)^2 = \frac{9}{4}$$

29. (A)

$$[A]_t = 1 \times e^{-kt} = e^{-3\times 33.33\times 10^{-2}} = e^{-0.999} = \frac{1}{e}$$

30. (C)

$$\begin{array}{lll} A \longrightarrow & B & + \quad C \\ Z & 0 & \quad\ \ 0 \\ Z-x & x & \quad\ \ x \\ 0 & Z & \quad\ \ Z \end{array}$$

$2Z + 3Z = b \quad \Rightarrow \quad 5Z = b$

$(Z-x) + 2x + 3x = a$

$\Rightarrow \quad Z + 4x = a$

$4Z - 4x = b - a \qquad (Z-x) = \dfrac{b-a}{4}$

$$k = \frac{1}{t}\ln\left(\frac{\frac{b}{5}}{\frac{b-a}{4}}\right)$$

31. (A)

$A \longrightarrow nC$

$$[A]_0 - \frac{7[A]_0}{8} = \frac{7[A]_0}{8}n \Rightarrow \frac{[A]_0}{8} = \frac{7[A]_0}{8}n$$

$$\Rightarrow \quad n = \frac{1}{7} \qquad \text{or} \qquad \frac{1}{n} = 7.$$

32. $(A \to p, r)$; $(B \to p, r, s)$; $(C \to q)$; $(D \to p, r, s)$

(A) IInd order reaction

(B) & (D) Ist order reaction

(C) zero order reaction

33. $(A \to p, q)$; $(B \to p, r, s)$; $(C \to s)$; $(D \to p, q)$

34. $(A \to q)$, $(B \to s)$, $(C \to r)$, $(D \to p)$

35. Arrhenius equation $k = Ae^{-E_a/RT}$

$$\text{or } \log_{10} k = \log A - \frac{Ea}{2.303RT}$$

Conparing the given equation with equation (i),

$$\frac{Ea}{2.303RT} = \frac{1.25\times 10^4\,(K)}{T}$$

$\Rightarrow \quad Ea = 2.303 \times 1.25 \times 10^4 \times 8.3 = 238936.25\ \text{J mol}^{-1}$

$$k = \text{antilog}\left[12.37 - \frac{1.25\times 10^4}{750}\right] = \text{antilog}\,(-4.3)\ \text{sec}^{-1}$$

$= 5 \times 10^{-5}\ \text{sec}^{-1}$

$\therefore\ Eak = 238936.25 \times 5 \times 10^{-5} = 11.95 \Rightarrow 12$

Hence Ans. **12**

36.

t :	0	5	15	35
[A] :	1	0.5	0.25	0.125

IInd order of the reaction

Ans. 2

37. $\dfrac{dx(1+bx)}{(a-x)} = Kdt$

$$dx\frac{[1-b(a-x)+ab]}{(a-x)} = Kdt$$

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

$-(1+ab)\log(a-x) - bx = Kt - (1+ab)\log a$

$$Kt = (1+ab)\log\frac{a}{(a-x)} - bx$$

$$\text{at } t = t_{1/2} \qquad x = \frac{a}{2}$$

$$K_{1/2} = (1 + ab)\log\frac{a}{a-\frac{a}{2}} - \frac{b.a}{2} = (1 + ab)\log 2 - \frac{ba}{2}$$

$$= \log 2 + ab\log 2 - ba \times 0.5$$

$$t_{1/2} = \frac{\log 2 + ab(\log 2 - 0.5)}{K}$$

38. (a) It is obvioius that $t_{1/2}$ is inversely proportional to the initial concentration .

Thus the reaction is of order 2.

$$K = \frac{1}{t}\left(\frac{1}{a-x} - \frac{1}{a}\right)$$

When $(a-x) = \frac{a}{2}$, $t = t_{1/2}$ we have $Kt_{1/2} = \frac{1}{a}$

$$\therefore K = \frac{1}{at_{1/2}} = \frac{1}{0.1 \times 135}\ \text{atm}^{-1}\,\text{min}^{-1}$$

(b) We may write, viscosity = η = (constant) $e^{-\frac{E_a}{RT}}$

$$\therefore \ln\eta = \ln(\text{constant}) - \frac{E_a}{RT}$$

$$\frac{d\ln\eta}{dT} = \frac{E_a}{RT^2};\ \frac{1}{\eta}\frac{d\eta}{dT} = \frac{E_a}{RT^2}$$

The left hand side of this equation is the fractional change of viscosity per degree-temperature change.

This is given as 0.02 deg^{-1}.

$$\therefore 0.02 = \frac{E_a}{1.987 \times (298)^2}$$

$E_a = 0.02 \times 1.987 \times (298)^2$ cal/mol

Ea = 3529 cal mol

39. $k = \frac{1}{30\,\text{min}}\ \ln$

$$\left\{\frac{400-200}{400-375}\right\} = \frac{1}{30\,\text{min}}\ln\left\{\frac{200}{0.25}\right\} = \frac{\ln 2}{T_{1/2}}$$

$$T_{1/2} = (30\ \text{min})\ \frac{\ln 2}{\ln 8} = 10\ \text{min}$$

So, we will have

Time (min)	t = 0	10	30
Pressure (in mm of Hg)	200	300	375
Volume of $KMnO_4$ consumed (ml)	40	2	5

Ans. **(a) 40, (b) 300, (c) 375, (d) 5**