

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

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

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

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

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

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

$$\text{So } k = 2k_1$$

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

$$k_1' = 2k_1$$

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

$$k_1'' = 2K_1$$

4. $xA \longrightarrow yB$

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

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

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

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

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

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

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

$$= 20 \text{ gram/min}$$

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

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

$$r_1 = K[1]^1[1]^2 = 1 \times 10^{-2} \quad (K = 1 \times 10^{-2})$$

$$r_1 = K \left[\frac{1}{2} \right] \left[\frac{1}{2} \right]^2 = 1 \times 10^{-2} \times \frac{1}{8} = 1.25 \times 10^{-3}$$

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

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

$$C_t = C_0 e^{-Kt} \Rightarrow C_t = C_0 e^{-K \times \frac{1}{K}}$$

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

11. $C_t = C_0 e^{-Kt}$

According to question

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

$$C_A e^{-K_A t} = C_B e^{-K_B t}$$

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

$$4 = e^{\left[\frac{\ln 2}{5} - \frac{\ln 2}{15} \right] \times t} \Rightarrow \ln 4 = \left[\frac{\ln 2}{5} - \frac{\ln 2}{15} \right] t$$

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

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

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

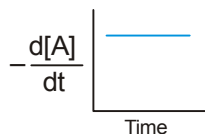
13. time Total for drop to disappears $(a_0 - a_t) = kt$

$$a_t = 0$$

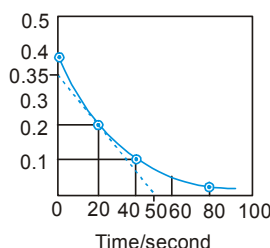
$$\frac{3.0 \times 10^{-6}}{(0.05 \times 10^{-3}) \times 1.0 \times 10^7} = t_{100\%} \Rightarrow t_{100\%} = 6 \times 10^{-9} \text{ sec}$$

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 $= \frac{dy}{dx} = \frac{0.35}{50} = 7 \times 10^{-3}$



17. $A + B \longrightarrow C$
 $t=0$ $a=0.1 \text{ M}$ $b=0.2 \text{ M}$ 0
 $t=100\text{s}$ $a-x$ $b-x$ x
 From question, $r = k[A][B]$ and hence

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

$$\text{or } 10^{-3} \times 100 = \frac{1}{0.2-0.1} \times 2.303 \times \log \frac{0.1(0.2-x)}{0.2(0.1-x)}$$

$$x \approx 0.002$$

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

19. $A \rightarrow nB$
 $t=0$ A_0 0
 $t=t$ A_0-x nx

From graph

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

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

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

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

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

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

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

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

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

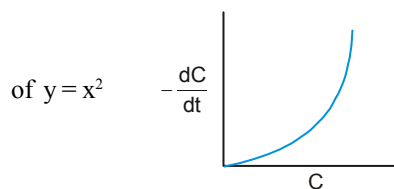
$$x = \frac{\log \left(\frac{r_1}{r_2} \right)}{\log \left(\frac{a_1}{a_2} \right)} = \frac{\log \frac{0.1}{0.1}}{\log \left(\frac{0.012}{0.024} \right)} = \frac{\log \left(\frac{1}{8} \right)}{\log \left(\frac{1}{2} \right)}$$

$$x = 3$$

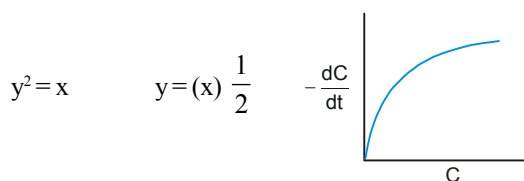
$$y = \frac{\log \frac{r_1}{r_3}}{\log \left(\frac{b_1}{b_2} \right)} = \frac{\log \left(\frac{0.1}{0.1} \right)}{\log \left(\frac{0.035}{0.070} \right)} = \frac{\log(1)}{\log \left(\frac{1}{2} \right)}$$

$$y = 0$$

26. dt is parabolic graph



So This the graph of second order



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

28. Initial pressure 65 105 y 185
 Half life 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

$$t_{1/2} = \frac{C_0}{2k} = \frac{P_0}{2k} \Rightarrow 290 = \frac{65}{2k} \Rightarrow k = \frac{65}{2 \times 290}$$

$$= 0.112 \text{ mm of Hg/sec}$$

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

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

$$\Rightarrow y = 150 \text{ mm of Hg}$$

29. $\text{NH}_4\text{NO}_2(\text{aq}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$

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

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

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

31. $\text{A}(\text{s}) \longrightarrow 2\text{B}(\text{g}) + \text{C}(\text{g})$

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

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

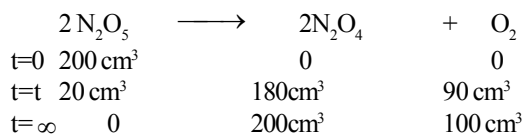
$$\frac{1}{20} \ln \left[\frac{225}{225 - 150} \right] \Rightarrow \frac{1}{20} \ln \left(\frac{225}{75} \right) = 0.05 \ln 3$$

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

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

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

$$33. k t = \ln \left(\frac{C_0}{C_t} \right)$$



Initial volume of $\text{N}_2\text{O}_5 = 200 \text{ cm}^3$.

because Max. volume of $\text{O}_2 = 100 \text{ cm}^3$.

$$\therefore K \times 500 = \ln \left(\frac{200}{20} \right) \Rightarrow k = \frac{\ln 10}{500} = \frac{2.303}{500}$$

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

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

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

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

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

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

$$42. \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$$

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

$$k_1 [\text{A}] [\text{B}] - k_2 [\text{C}] [\text{D}] = 0$$

$$k_1 [\text{A}] [\text{B}] = k_2 [\text{C}] [\text{D}]$$

$$[\text{A}] [\text{B}] = [\text{C}] [\text{D}]$$

$$0.4 \times 0.25 = 0.2 \times 0.5$$

$$1 = 1$$

$$44. \text{Equation : } \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$$

$$\text{Given, } \frac{dx}{dt} = 2 \times 10^7 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} [\text{Ag}^+] [\text{NH}_3]^2$$

$$- 1 \times 10^{-2} \text{ s}^{-1} [\text{Ag}(\text{NH}_3)_2]^+$$

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

$$2 \times 10^7 [\text{Ag}^+] [\text{NH}_3]^2 - 1 \times 10^{-2} [\text{Ag}(\text{NH}_3)_2]^+ = 0$$

$$\frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+] [\text{NH}_3]^2} = \frac{2 \times 10^7}{1 \times 10^{-2}} = 2 \times 10^9 \text{ L}^2 \text{ mol}^{-2}$$

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

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

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

at Y axes

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

at x axis

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

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

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

Rxn endothermic because $\Delta H(+)$

$$\Delta H = E_a - E_b$$

$$5 = 10 - E_b$$

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

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

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

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

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

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

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

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

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



Rate of decomposition

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

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

At equilibrium rate of decomposition = rate of formation

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

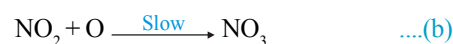
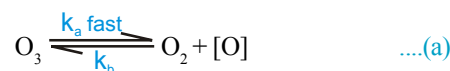
$$[A^*] = \frac{K_1}{K_2}[A]$$

58. For Rxn rate determining step is slowest step

Then in 1st Rxn

$$\text{Rate} = k[\text{NO}_2][\text{O}_3] \quad \dots(i)$$

But 2nd Rxn



Then for Rxn (a)

$$\frac{k_a}{k_b} = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} = k_{eq} \quad \dots(d)$$

by Rxn (b)

$$\text{Rate} = k[\text{NO}_2][\text{O}] \quad \dots(ii)$$

put value of $[\text{O}]$ from (d) to (ii)

$$\text{Rate} = k \frac{k_{eq}[\text{O}_3]}{[\text{O}_2]} \times [\text{NO}_2]$$

$$\text{Rate} = \frac{k_1[\text{NO}_2][\text{O}_3]}{[\text{O}_2]}$$

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

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

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

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

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.

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

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

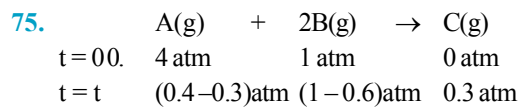
$$73. C_t = C_0 e^{-Kt}$$

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

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

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

t = 2 natural life time.



Since reaction is elementary.

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

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

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

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

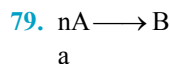
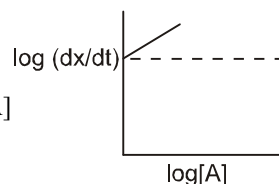
$$\frac{R_{(t=t)}}{R_{(t=0)}} = \frac{K[0.1][0.4]^2}{K[0.4][1]} = \frac{1}{25}$$

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

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

Slope = 2

Intercept = log k.



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

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

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

80. If ester 50% hydrolysed then

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

We can write

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

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

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

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

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

$$\text{or } V_{\infty} = 2 V_t - V_0$$

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

At 50% Inversion

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

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

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

$$r_0 = 2r_t - r_{\infty}$$



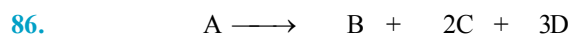
$$t=0 \quad 2P_0 \quad P_0$$

$$t=0 \quad 2 \text{ atm} \quad 1 \text{ atm} \quad 0$$

$$t=t \quad 0 \quad 0 \quad 2 \text{ atm}$$

$$2P_0 + P_0 = 3 \text{ atm}$$

$$P_0 = 1 \text{ atm}$$



Optical rotation –	θ_1	θ_2	θ_3
$t=0$	a	0	0

Optical rotation at $t=0$ is zero.

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

$t=\infty$	0	a	2a	3a
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Optical rotation at time $=\infty$ 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

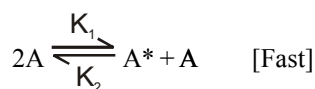
Part # 1 : Multiple Choice

1. $K = \frac{K_1 K_3}{K_2}$

$$Ae^{\frac{-(E_a)_{\text{overall}}}{RT}} = \frac{A_1 e^{-\frac{E_1}{RT}} \times A_3 e^{-\frac{E_3}{RT}}}{A_2 e^{-\frac{E_2}{RT}}}$$

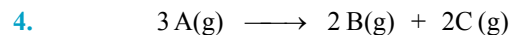
$$Ae^{\frac{-(E_a)_{\text{overall}}}{RT}} = \left(\frac{A_1 A_3}{A_2} \right) e^{-\frac{[E_1 + E_3 - E_2]}{RT}}$$

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



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

$$\text{rate} = K_3 [A^*] = \frac{K_1 K_3}{K_2} [A]$$



$$t=0 \quad P_0$$

$$t=20 \quad P_0 - x \quad \frac{2x}{3} \quad \frac{2x}{3}$$

$$t=\infty \quad \frac{2P_0}{3} \quad \frac{2P_0}{3}$$

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

$$P_0 = 3 \text{ atm.}$$

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

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

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

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

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



$$30 \quad 20 \quad -15$$

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

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

$$\therefore t_{1/2} = \frac{30 \ln 2}{\ln \frac{45}{35}} = 15 \text{ min}$$

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

$$t = 120 \text{ min}$$

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

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

$$\Rightarrow x = 22.5 - 15 = 7.5^\circ$$

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

Compare this with

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

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

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

$E_a = 9.212 \text{ k cal.}$

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

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

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

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

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

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

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

Rate = $k [\text{Zn}][\text{H}^+]^n$ we can write

by data $\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{Zn}]}{[\text{Zn}]} \left[\frac{1 \times 10^{-2}}{1 \times 10^{-3}} \right]^n = \frac{100}{1}$

Given $n = 2$

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

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

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

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

Rate remains and same.

(D) Similarly if conc. of H^+ doubled and $[\text{Zn}]$ constant

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

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

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

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

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

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

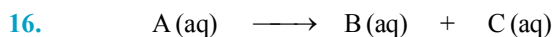
14. Over all order of Rxn = $\left(1 - \frac{1}{2} \right) = + \frac{1}{2}$

as SO_3 for Rate of Rxn slow down.

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

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

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



$t=0$ a 0 0

$t=t$ $a-x$ x x

$t=\infty$ 0 a a

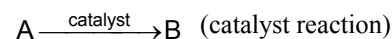
$(a-x) + 2x + 3x \propto n_1$

$a + 4x \propto n_1$

$2a + 3a \propto n_2$

$a \propto \frac{n_2}{5}$

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



$K = Ae^{-E_a/RT}$

$K_{\text{cat.}} = Ae^{-E_{a(\text{cat.})}/RT}$

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

$\frac{K_{\text{cat.}}}{K} = e^{\frac{8.314 \times 10^3}{8.314 \times 300}} = e^{3.33} = 28 \text{ times}$

20. We have,

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

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

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

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

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

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

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

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

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

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

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

26. A \longrightarrow Product

$$\text{We know, Rate} = K [\text{conc.}]^n$$

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

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

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

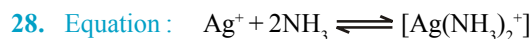
$$n = \frac{1}{2}$$

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

27. Rate of reaction independent of conc. of A

$$\text{Net Rxn Rate} = K_1 [A]^0 - K_2 [B]^1$$

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



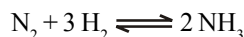
$$\text{Given, } \frac{dx}{dt} = (2 \times 10^7 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}) [Ag^+] [NH_3]^2 - (1 \times 10^{-2} \text{ s}^{-1}) [Ag(NH_3)_2^+]$$

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

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

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

29. Given Rxn



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

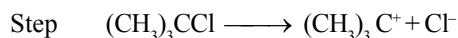
$$\text{when } \frac{dx}{dt} = 0 \text{ then } \frac{[N_2] [H_2]^3}{[NH_3]^2} = 10^{-5}$$

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



$$\text{Initial conc. } 1 \quad 1$$

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)

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

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

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 1st order Rxn and other all are properties of 2nd 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

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

$$0.50 - A_t = 0.025 \times 15$$

$$A_t = 0.125 \text{ M}$$

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

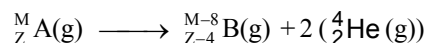
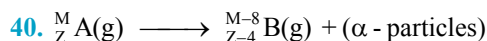
$$= \frac{2.303}{90} \text{ min}^{-1}$$

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

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

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

$$\text{Then Rate} = k[A_t] = \frac{.6932}{10} \times 2.5 = .06932 \times 2.5 = \mathbf{16}$$



$$\begin{array}{ccc} 1 \text{ mole} & 0 & 0 \end{array}$$

$$\begin{array}{ccc} \left(1 - \frac{3}{4}\right) & \frac{3}{4} & 2 \times \frac{3}{4} \end{array}$$

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

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

$$pV = nRT$$

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

$$p = 61.5 \text{ atm}$$

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

$$\text{Then } N_0 = (23 - 3) = 20 \text{ dps}$$

$$N_t = 10 \text{ dps}$$

The half life = 10 minutes

In next 10 minute $N_t = 5 \text{ dps}$

Then value with error = $(5 + 3) = 8 \text{ dps}$.

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

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

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

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

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

$$E_a = \frac{2.303 RT_1 T_2}{(T_2 - T_1)} \log \left(\frac{k_{40^\circ\text{C}}}{k_{0^\circ\text{C}}} \right)$$

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

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

compare this by

$$y = mx + c$$

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

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

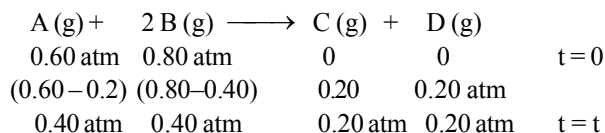
$$E_a = R = 2 \text{ cal}$$

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

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

Rate 2 = $k[A_1][B_1]^2$ (ii)

Given Rxn



Put value of pressure of $t = t$ in rate equation (ii)

$$\text{Rate 2} = k[.40][.40]^2$$

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

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

Given, pH change from 2 to 1

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

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

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

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 $\text{Rate} = k[Zn][H^+]^a$

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

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

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

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

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

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

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

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

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

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

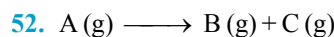
$$\frac{2}{1} = \frac{[H^+]_A}{[H^+]_B} = \text{strength of } \frac{[\text{Acid A}]}{[\text{Acid B}]}$$

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

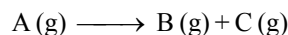
$$t_{av} = \frac{1}{k_1}$$

Given $t = 2 t_{av} = \frac{2}{k_1}$

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



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



$$\begin{array}{ccc} 100 & 0 & 0 \\ (100-P) & P & P \\ 100-P+P+P & = & 120 \\ (100+P) & = & 120 \end{array} \quad \begin{array}{l} t=0 \\ t=10 \text{ min.} \end{array}$$

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

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

53. Rate constant change on changing temperature .

54. We know

$$-\frac{d(\text{BrO}_3^-)}{dt} = -\frac{1}{5} \frac{d(\text{Br}^-)}{dt} = -\frac{1}{6} \frac{d(\text{H}^+)}{dt} = +\frac{d(\text{Br}_2)}{dt}$$

Then by this relation $\frac{d(\text{Br}_2)}{dt} = -\frac{3}{5} \frac{d(\text{Br}^-)}{dt}$

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, **1st order Rxn.**

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

57. According to above data.

suppose rate law, $\frac{dx}{dt} = k [\text{CH}_3\text{COCH}_3]^a [\text{Br}_2]^b [\text{H}^+]^c$

by data (i) and (ii) conc. of $[\text{Br}_2]$ increased 2 times and conc. of $[\text{CH}_3\text{COCH}_3]$ and $[\text{H}^+]$ constant rate remains same. Then zero order wrt Br_2 .

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

Similarly 1st order wrt CH_3COCH_3

Then, $\frac{dx}{dt} = k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$

58. Rate = $k [\text{conc}]^n \longrightarrow$ Independent of conc. of A.

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

60. Rate determining step is slow step

Then Rate = $k_2 [\text{SO}_3 \cdot 2 \text{H}_2\text{O}] \dots\dots(i)$

We know by fast equation

$$\frac{k_1}{k_{-1}} = \frac{[\text{SO}_3 \cdot 2 \text{H}_2\text{O}]}{[\text{SO}_3][\text{H}_2\text{O}]^2}$$

$$[\text{SO}_3 \cdot 2 \text{H}_2\text{O}] = \frac{k_1}{k_{-1}} [\text{SO}_3] [\text{H}_2\text{O}]^2 \dots\dots(ii)$$

put the value of $[\text{SO}_3 \cdot 2 \text{H}_2\text{O}]$ from (ii) to (i)

$$\text{Rate} = k_2 \times \frac{k_1}{k_{-1}} [\text{SO}_3] [\text{H}_2\text{O}]^2$$

$$\text{Rate} = k [\text{H}_2\text{O}]^2 [\text{SO}_3]$$

61. $\text{H}_2\text{O} + \text{O} \longrightarrow 2 \text{OH}$ $\Delta H = 72 \text{ kg/mole}$

and $E_a = 77 \text{ Kg/mole}$

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

$$72 = 77 - E_b$$

$$E_b = 5 \text{ KJ/mole}$$

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

we know that for any reaction

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

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

$$\frac{dk}{dT} = \frac{k_2 \frac{d}{dT}(k_1 k_3) - k_1 k_3 \frac{dk_2}{dT}}{K_2^2}$$

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

$$k \cdot \frac{E_a}{RT^2} = \frac{k_1 k_3}{k_2} \cdot \frac{E_{a3}}{RT^2} + \frac{k_3 k_1}{k_2} \cdot \frac{E_{a1}}{RT^2} - \frac{k_1 k_3}{k_2} \cdot \frac{E_{a2}}{RT^2}$$

$$E_a = E_{a3} + E_{a1} - E_{a2} \\ = (20 + 40 - 30) = 30 \text{ kJ/mol}$$

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

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

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

67. $2A + B \longrightarrow C$

$$t = 0 \quad 2a \quad a \quad 0$$

$$t = t \quad 2a - 2x \quad a - x \quad x$$

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

$$\Rightarrow [C] = 2kt$$

$$\text{unit of } k = \text{Ms}^{-1}$$

$$[A] = 2(a-x) \text{ and } [C] = x$$

$$[B] = (a-x).$$

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

$$t = 0 \quad 400 \quad 0 \quad 0$$

$$t = 20 \text{ min} \quad 400 - p \quad 2p \quad p$$

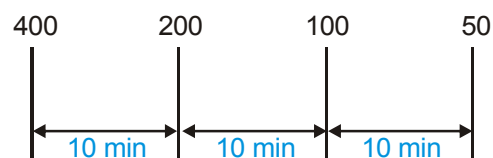
$$\text{Given } 400 - p + 2p + p = 1000$$

$$400 + 2p = 1000$$

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

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

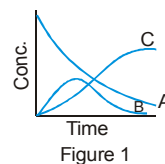
$$T_{1/2} = 10 \text{ min}; \quad \text{Value of } K = 0.0693 \text{ min}^{-1}$$



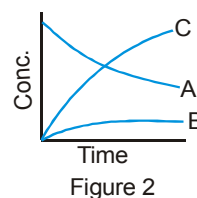
After 30 min Partial Pressure of A is 50 mm, After 30 min Partial Pressure of B is 700 mm

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

71. For figure-1 :



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



For figure-2 :

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

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 $K = Ae^{-E_a/RT}$ 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) $r = k[A][B]$

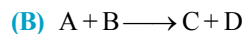
i.e. IInd order reaction

unit of $k = \text{mol}^{-1} \text{ l} \text{ t} \text{ time}^{-1}$

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

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

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

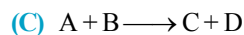


$$r = k_2 [B]^0 [A] = k_2 [A]$$

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

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

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

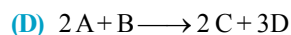


$$r = k_3 [A]^0 [B]^0$$

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

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

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



$$r = K_3 [A]^0 [B]^0$$

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

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

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

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

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

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

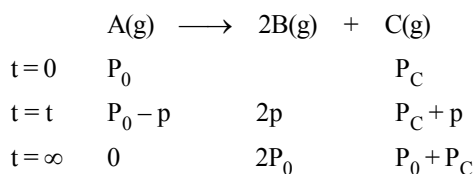
(D) $t_{1/2} \propto (a)^{1-n}$ or $(1-n) = \frac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''}$

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

Part # II : Comprehension

Comprehension : 2

(1 to 3)



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

$$3P_C = P_0 + P_C$$

$$2P_C = P_0$$

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

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

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

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

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

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

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

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

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

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

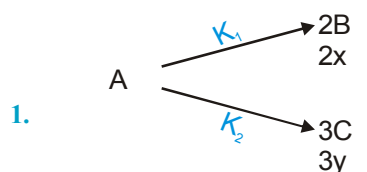
$$P_\infty = 3P_0 + P_C = 35$$

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

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

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

Comprehension : 3



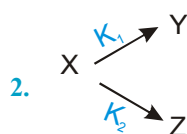
$$t = 0 \text{ a}$$

$$t - t \text{ a} - x - y$$

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

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

$$a = a$$



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

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

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

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

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

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

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

$$= 1 \times 10^{-7} \text{ m/sec}$$

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

3. (III) $\text{Rate I} = \text{Rate II}$

$$k_1 [A] [B] = k_1 [A] \Rightarrow B = \frac{k_1}{k_1} = 10 \text{ M}$$

Comprehension : 5

Sol. (1 to 3)

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

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

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

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)

$1.32 \times 10^{-4} = k [1.10]^a [0.05]^b$ (ii)

$2.6 \times 10^{-4} = k [1.10]^a [1.10]^b$ (iii)

$1.02 \times 10^{-3} = k [2.20]^a [1.10]^b$ (iv)

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

By (iii) and (iv) we find $a = 2.97 \approx 3$.

Then $\text{Rate} = k [A]^3 [B]^1$

3. (III) $\text{Rate } 1.32 \times 10^{-4} = k [1.10]^3 [0.05]$

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

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

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

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.

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

Also rate of reaction,

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

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

$$\therefore P = CRT$$

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

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

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

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

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

$$4. \text{ (A) Rate} = -\frac{dC_A}{dt} = K C_A^a$$

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

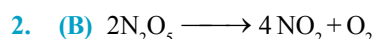
$$\therefore \log K = 0.6$$

$$K = 3.98 \text{ time}^{-1} \text{ and } a = 1 = \tan \theta \text{ } (\theta = 45^\circ).$$

Comprehension : 7

Sol. (1 to 4)

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



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

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

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

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

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

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

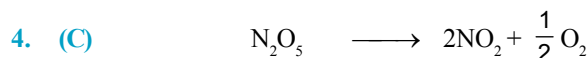
$$3. \text{ (B) } \frac{d[O_2]}{dt} = 16 \text{ g/hr} = \frac{16}{32} \text{ mol hr}^{-1} = \frac{1}{2} \text{ mol hr}^{-1}$$

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

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

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

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



Initial mole	4	0	0
moles after diss	0	8	2

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

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{6.2 \times 10^{-4}} = 1117.7 \text{ sec but it depends}$$

upon temperature as K also depends upon temperature.

$$t_{40\%} = \frac{2.303}{6.2 \times 10^{-4}} \log \frac{100}{60} = 822.98 \text{ sec}$$

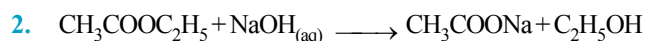
$$\text{Rate} = K[N_2O_5]; \text{ Thus } r_1 = K[N_2O_5]$$

If V is doubled the concentration becomes half

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

EXERCISE - 4

Subjective Type



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

$$\text{At time } t = 0 \quad \frac{b \times 100}{1000} = \frac{0.05 \times 75}{1000}$$

$$\text{so } b = \frac{0.05 \times 75}{100} \Rightarrow b = \frac{0.15}{4}$$

$$\text{At time } t = 30 \text{ min} \quad \frac{(b-x) \times 50}{1000} = \frac{0.05 \times 25}{1000}$$

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

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

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

$$(b-a) = \frac{0.05}{4}$$

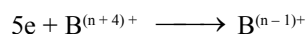
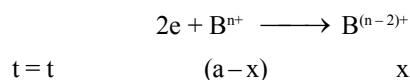
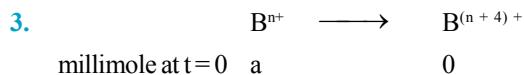
$$a = b - \frac{0.05}{4} = \frac{0.15}{4} - \frac{0.05}{4} = \frac{0.1}{4}$$

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

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

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

Ans. $k = 0.736 \text{ litre/mol/minute}$



Let normality be N for reducing agent.

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

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

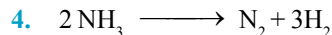
$$\text{at } t=t \quad (a-x) \times 2 + x \cdot 5 = N \times 32$$

$$\therefore 3x = 7N$$

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

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

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



$$r = k [\text{NH}_3]^0 = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = +\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$= 2.5 \times 10^{-4} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{d[\text{N}_2]}{dt} = 2.5 \times 10^{-4}$$

$$\frac{d[\text{H}_2]}{dt} = 7.5 \times 10^{-4}$$

$$(d) \frac{-d[\text{NH}_3]}{dt} = \frac{k_1 [\text{NH}_3]}{1 + k_2 [\text{NH}_3]}$$

(i) NH_3 is very – very Less $\frac{-d[\text{NH}_3]}{dt} = k_1 [\text{NH}_3]$
 \longrightarrow First order

(ii) NH_3 is very – very High $\frac{-d[\text{NH}_3]}{dt} = \left(\frac{k_1}{k_2} \right)$
 \longrightarrow zero order

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

During any experiment pH is constant

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

Since Half is independent of the Initial conc. of A

Hence $a = 1$

First order w.r.t A. Now k' is First order rate

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

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

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

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

8. ℓ – potassium chromo - oxalate \rightleftharpoons d potassium chromo oxalate

$$\begin{array}{ccc} t=0 & a & 0 \\ t=t_{eq.} & (a-x_{eq.}) & x_{eq.} \end{array}$$

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

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

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

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

$$2K_f = 5.42 \times 10^{-4}$$

$$K_f = K_b = 2.71 \times 10^{-4}$$

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

$$\begin{array}{ccc} t=0 & a & 0 \\ t=60 \text{ min} & 0.8a & \\ t=90 \text{ min} & 0.40a & \\ t=100 \text{ min} & 0.10a & \end{array}$$

In absence of catalyst

$$K = \frac{2.303}{60} \log \frac{a}{0.8a} = \frac{2.303}{60} \log \left(\frac{5}{4} \right) \quad \dots(i)$$

For I^{st} catalyst

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

$$\frac{(K_{cat.})_{I^{\text{st}}}}{K} = \frac{\frac{2.303}{30} \log 2}{\left(\frac{2.303}{60} \right) \times \log \left(\frac{5}{4} \right)} = \frac{2 \log 2}{\log 5 - \log 4} = \frac{2 \times 0.30}{0.1}$$

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

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

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

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

$$E_a = 80 - \frac{2.303 \times 0.793 \times 8.314 \times 300}{1000} = 80 - 4.56 = 75.44 \text{ kJ.}$$

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

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

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

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

$$+ K_c[NO][NO_3] \quad \dots(2)$$

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

$$[NO] = \frac{K_b[NO_2]}{K_c} \quad \dots(3)$$

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

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

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

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

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

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

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

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

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

$$K = \frac{1}{1} \ln \left(\frac{70}{70-x_1} \right) = \frac{1}{4} \ln \left(\frac{70}{70-x_2} \right)$$

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

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

$$x_2 = 58\%$$

so % of A remaining = 42%.

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

For 1st reaction

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

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

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

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

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

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

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

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

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

$$16. \frac{d[\text{HBr}]}{dt} = K_2[\text{H}_2][\text{Br}] + K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}]$$

$$\frac{d[\text{HBr}]}{dt} = K_2[\text{H}_2][\text{Br}] + K_3[\text{H}][\text{Br}_2] - K_4[\text{HBr}][\text{H}]$$

$$\text{Now, } \text{Br}_2 \xrightleftharpoons[K_5]{K_1} 2\text{Br}$$

$$\frac{K_1}{K_5} = \frac{[\text{Br}]^2}{[\text{Br}_2]}$$

$$\text{so } [\text{Br}] = \left(\frac{K_1}{K_5} \right)^{1/2} [\text{Br}_2]^{1/2} \quad \dots(1)$$

At steady state,

$$\frac{d[\text{H}]}{dt} = K_2[\text{Br}][\text{H}_2] - K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}] = 0$$

$$\text{So, } [\text{H}] = \frac{K_2[\text{H}][\text{Br}]}{K_3[\text{Br}_2] + K_4[\text{HBr}]}$$

$$\frac{d[\text{HBr}]}{dt} = K_2[\text{H}_2][\text{Br}] + \left[K_3[\text{Br}_2] - K_4[\text{HBr}] \right]$$

$$\frac{K_2[\text{H}_2][\text{Br}]}{K_3[\text{Br}_2] + K_4[\text{HBr}]}$$

$$\frac{d[\text{HBr}]}{dt} = K_2[\text{H}_2][\text{Br}] \left[1 + \frac{K_3[\text{Br}_2] - K_4[\text{HBr}]}{K_3[\text{Br}_2] + K_4[\text{HBr}]} \right]$$

$$\frac{d[\text{HBr}]}{dt} = K_2 \left(\frac{K_1}{K_5} \right)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2}$$

$$\left[\frac{K_3[\text{Br}_2] + K_4[\text{HBr}] + K_3[\text{Br}_2] - K_4[\text{HBr}]}{K_3[\text{Br}_2] + K_4[\text{HBr}]} \right]$$

$$\frac{d[\text{HBr}]}{dt} = K_2 \left(\frac{K_1}{K_5} \right)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2} \left[\frac{2K_3[\text{Br}_2]}{K_3[\text{Br}_2] + K_4[\text{HBr}]} \right]$$

$$\frac{d[\text{HBr}]}{dt} = 2K_2 \left(\frac{K_1}{K_5} \right)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2} \left[\frac{1}{1 + \frac{K_4[\text{HBr}]}{K_3[\text{Br}_2]}} \right]$$

$$\text{So, } \frac{d[\text{HBr}]}{dt} = \frac{2K_2 \left(\frac{K_1}{K_5} \right)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{K_4[\text{HBr}]}{K_3[\text{Br}_2]}}$$

$$18. \therefore k = Ae^{-E_a/RT}$$

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

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

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

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

$$\log_e \frac{k_2}{k_1} = \frac{75}{RT} = \frac{75 \times 10^3}{8.314 \times 293} \quad (\Delta H \text{ in kJ})$$

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

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

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

$$19. \lambda_A = \lambda_1 + \lambda_2 = 1.5 \times 10^{-5} + 5 \times 10^{-6} \\ = 20 \times 10^{-6} \text{ sec}^{-1}$$

$$[C]_t = \frac{2\lambda_2}{\lambda_1 + \lambda_2} [A]_0 [1 - e^{-(\lambda_1 + \lambda_2)t}] = \frac{2 \times 5 \times 10^{-6}}{20 \times 10^{-6}} \times 0.25 \\ [1 - e^{-(20 \times 10^{-6} \times 5 \times 3600)}] = 3.7 \times 10^{-2} \text{ M.}$$

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

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

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

$$\text{and } (t_{1/2})_B = \frac{1}{a \cdot k_B} \quad \dots (iv)$$

where a is initial concentration.

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

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

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

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

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

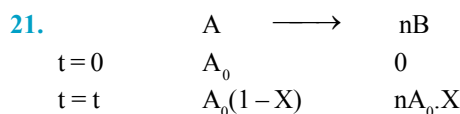
$$\therefore \text{ From Eqs. (v) and (vi), } \frac{r_A}{r_B} = \frac{0.693a}{a} = 0.693$$

(b) After lapse of I half, the new rates are r_A^t and r_B^t

$$r_A^t = k_A \times \frac{a}{2}; r_B^t = k_B \times \left(\frac{a}{2}\right)^2$$

$$\therefore \frac{r_A^t}{r_B^t} = \frac{k_A}{k_B} \times \frac{2}{a} \quad \dots (vii)$$

$$\text{By Eqs. (vi) and (vii) } \frac{r_A^t}{r_B^t} = 0.693 \times a \times \frac{2}{a} = 1.386$$



At intersection point O obtained after time t ,

$$[A] = [B]$$

$$\therefore A_0(1-X) = nA_0X$$

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

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

$$22. (i) \text{ Rate of forward reaction} = 2.0 \times 10^{-4} [\text{Cu}(\text{NH}_3)_4]^{2+} \\ \text{Rate of backward reaction} = 3.0 \times 10^{-5} \\ [\text{Cu}(\text{NH}_3)_3 \text{H}_2\text{O}]^{2+} [\text{NH}_3]$$

$$(ii) \text{ Therefore, } k_f = 2.0 \times 10^{-4} \text{ \& } k_b = 3.0 \times 10^{-5}$$

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

equilibrium constant is very less therefore backward reaction is predominant.

$$23. \text{ For reaction (a) : } K_1 = A_1 e^{-E_a/RT} \text{ or } 2.79 \times 10^{-3}$$

$$= A_1 e^{-\frac{12 \times 10^3}{RT}} \quad \dots (i)$$

$$\text{For reaction (b) : } K_2 = A_2 e^{-E_a/RT} \text{ or } 1.52 \times 10^{-4}$$

$$= A_2 e^{-\frac{24.5 \times 10^3}{RT}} \quad \dots (ii)$$

$$\text{By Eq. (i)} \quad A_1 = \frac{2.79 \times 10^{-3}}{\exp\left(-\frac{12 \times 10^3}{2 \times 510}\right)} = \frac{2.79 \times 10^{-3}}{7.8 \times 10^{-6}}$$

$$= 3.5 \times 10^2$$

$$\text{By Eq. (ii)} \quad A_2 = \frac{1.52 \times 10^{-4}}{\exp\left(-\frac{24.5 \times 10^3}{2 \times 510}\right)} = \frac{1.52 \times 10^{-4}}{3.7 \times 10^{-11}}$$

$$= 4.1 \times 10^6$$

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.,

$$A_1 e^{-E_a/Rt} = A_2 e^{-E_a/Rt}$$

$$3.5 \times 10^2 \times e^{-\frac{12 \times 10^3}{RT}} = 4.1 \times 10^6 \times e^{-\frac{24.5 \times 10^3}{RT}}$$

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

$$\text{or} \quad \frac{10^3}{RT} \times 12.5 = 9.37$$

$$\therefore T = \frac{12.5 \times 10^3}{9.37 \times 2} = 667 \text{ K}$$

$$\therefore T = 394^\circ \text{C}$$

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) \therefore 0.1 mole of A gives to 0.2 moles of B in a given time and thus,

$$n = 2$$

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

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

$$= 1.2 \text{ mole litre}^{-1}$$

(iii) Initial rate of conversion of A = changes in conc. of

$$A \text{ during 1 hour} = \frac{0.1}{1} = 0.1 \text{ mole litre}^{-1} \text{ hour}^{-1}$$



$$t = 30 \left[0.002 - \frac{0.002 \times 1}{100} \right] \left[0.3 - \frac{0.002 \times 1}{100} \right]$$

For II order reaction having [A] \neq [OH⁻]

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

$$\text{Using, } k = \frac{2.303}{30 \times (0.002 - 0.3)} \log$$

$$\frac{0.3 \times \left[0.002 - \frac{0.002 \times 1}{100} \right]}{0.002 \times \left[0.3 - \frac{0.002 \times 1}{100} \right]}$$

$$k = 1.12 \times 10^{-3} \text{ litre mol}^{-1} \text{ sec}^{-1}$$

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

Hint : Use hit and trial method.

Case I : $a \propto 200 \text{ mm}$;

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

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

$$= 1.307 \times 10^{-2} \text{ minute}^{-1}$$

Case II : $a \propto 200 \text{ mm}$;

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

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

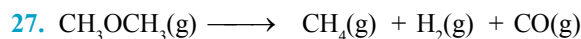
$$\therefore k_2 = \frac{2.303}{100} \log \frac{200}{200-146}$$

$$= 1.309 \times 10^{-2} \text{ minute}^{-1}$$

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

$$(b) k = \frac{k_1 + k_2}{2} = \frac{(1.309 + 1.307) \times 10^{-2}}{2} = 1.308 \times 10^{-2}$$

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



Pressure at $t = 0$ 0.40

Pressure at $t = 12$ min

$$(0.40 - P) \quad P \quad P \quad P$$

For ideal gas behaviour moles \propto pressure

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

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

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

$$\therefore P = 0.175 \text{ atm}$$

$$\begin{aligned} \text{Thus, total pressure after 12 minutes} &= 0.40 - P + P + P + P \\ &= 0.40 + 2P \\ &= 0.40 + 2 \times 0.175 = \mathbf{0.75 \text{ atm}} \end{aligned}$$

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

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

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

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

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

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

$$= \mathbf{13.95 \text{ hour}}$$

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

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

$$\therefore \text{Volume of } \text{N}_2\text{O} \text{ formed at STP} = 0.099 \times 22.4 = \mathbf{2.2117 \text{ litre}}$$

29. Let $\text{rate} = K [\text{CH}_3\text{COF}]^a [\text{H}_2\text{O}]^b$

It is given that in case I : $[\text{H}_2\text{O}] \gg [\text{CH}_3\text{COF}]$

and in case II : $[\text{H}_2\text{O}] \ll [\text{CH}_3\text{COF}]$

Thus, according to ostwald isolation method, we can assume $[\text{H}_2\text{O}]$ in excess in case I and $[\text{CH}_3\text{COF}]$ in excess case II.

Thus, for case I :

Using I order for CH_3COF , we have

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

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

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

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

Thus, order with respect to $[\text{CH}_3\text{COF}]$ 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 $[\text{H}_2\text{O}]$ is one or $b = 1$

Now $\text{rate} = K_t = [\text{CH}_3\text{COF}]^1 [\text{H}_2\text{O}]^1$

Also $\text{rate} = K [\text{CH}_3\text{COF}]^1 [\text{H}_2\text{O}]^0$ case I

$$\therefore \frac{K_t}{k} = [\text{H}_2\text{O}]^1$$

$$\begin{aligned} \text{or } K_t &= K \times [\text{H}_2\text{O}]^1 \\ &= 0.0154 \times 1.0 = \mathbf{1.54 \times 10^{-2} \text{ min}^{-1}} \end{aligned}$$

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

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

$$\text{By Eqs. (i) and (ii) } \frac{t_{99\%}}{t_{90\%}} = \frac{\log 100}{\log 10} = 2$$

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

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

	A	→	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 ∝ pressure at that time

$$a \propto P_0 \quad t = 0 \quad \dots (i)$$

$$\therefore a + 2X \propto 264 \quad t = 14 \text{ minute} \quad \dots (ii)$$

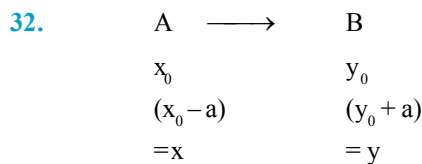
$$3a \propto 264 \quad t = \infty \quad \dots (iii)$$

(a) ∴ By Eqs. (i) and (ii) $P^0 = 150 \text{ mm}$

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

$$K = \frac{2.303}{14} \log \frac{150}{150 - 57} = 3.415 \times 10^{-2} \text{ min}^{-1}$$

$$(c) t_{1/2} = \frac{0.693}{K} = \frac{0.693}{3.415 \times 10^{-2}} = 20.29 \text{ min}$$



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

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

$$\text{Put } x_0 - a = x$$

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

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

$$= K[x_0 y_0 + ax_0 - ay_0 - a^2]$$

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

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

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

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

On integrating,

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

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

$$\text{at } t = 0, \quad a = 0$$

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

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

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

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

$$\text{at } T (T^\circ \text{K}) = (273 + 43.3) = 316.3 \text{ K}$$

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

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

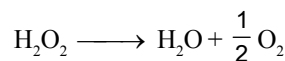
$$K = 10^{22}$$

Then half life period

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

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

34. Decomposition of H_2O_2 1st order (Rxn)



Then we know

$$K = Ae^{\frac{-E_a}{RT}}$$

For uncatalysed Rxn

$$K_1 = Ae^{\frac{-E_a}{RT}} \quad [T = 300 \text{ K}, R = 2]$$

$$K_1 = Ae^{\frac{-18 \times 10^3}{2 \times 300}} \quad \dots (i)$$

and for catalysed Rxn

$$K_2 = Ae^{\frac{-6 \times 10^3}{2 \times 300}} \quad \dots (ii)$$

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.

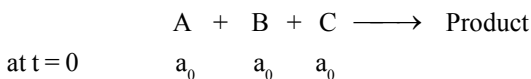
35. We know, Rate = $K [\text{conc}]^n$ for n^{th} order Rxn.

Then,
$$\frac{\text{Rate}_2}{\text{Rate}_1} = \left(\frac{\text{conc}_2}{\text{conc}_1} \right)^n$$

given, $\text{Rate}_2 = \text{Rate}_1$, $\text{conc}_2 = (\text{conc}_1 \times 1.5)$
 $2.25 = (1.5)^n$

$n = 2$ second order Rxn

36. (a) Rxn zero order w.r.t. to A then.
 when half of A reacted



$$\text{at } t = 1000 \text{ sec. } \frac{a_0}{2} \quad \frac{a_0}{2} \quad \frac{a_0}{2}$$

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.

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

$$a_t = 0 \quad \text{zero fraction left.}$$

- (b) 2^{nd} 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.

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

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

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

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

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

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

37. $\text{CH}_3\text{COCH}_3(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CO}(\text{g})$

$$t = 0 \quad .5$$

$$t = t \quad .4$$

Then by given data

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

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

$$t = 26.07 \text{ sec}$$

38. For $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$

$$x \propto V_t,$$

$$a \propto V_\infty$$

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

Then for 1^{st} 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, $V_\infty = 108.23 \text{ mL}$

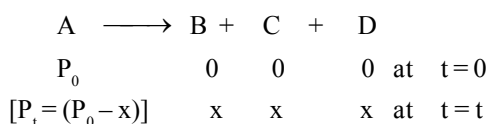
39. $A \longrightarrow B + C + D$.

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.



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.

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

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

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

From (i) and (ii) data.

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

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

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

$$n = 2 \text{ II}^{\text{nd}} \text{ order Rxn.}$$

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

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

Given :

$$A_t - A_0 e^{-k_1 t} \quad \dots (i)$$

$$B_t - B_0 e^{-k_2 t} \quad \dots (ii)$$

$$A_0 = B_0$$

$$A_t = 4B_t$$

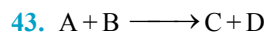
by (i)/(ii)

$$\frac{4B_t}{B_t} = \left(\frac{B_0 e^{-k_1 t}}{B_0 e^{-k_2 t}} \right)$$

$$4 = e^{(k_2 - k_1)t}$$

$$\ln 4 = (k_2 - k_1) t$$

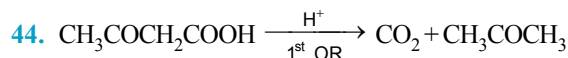
$$t = \frac{\ln 4}{(k_2 - k_1)} = \frac{\ln 4}{(k_2 - k_1)} = \frac{0.6932}{18} - \frac{0.6932}{54} = 53 \text{ min.}$$



Second order W.R.T.A

Then $t_{1/2} = \frac{1}{k a_0}$

$$t_{1/2} = \frac{1}{0.622 \times 4.10 \times 10^{-2}} = 39.2 \text{ min.}$$



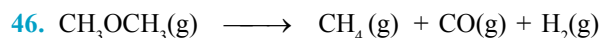
45. (i) $r = k[\text{O}][\text{O}_2]$

$$0.15 = 1.5 \times 10^7 [\text{O}][\text{O}_2]$$

$$0.15 = 1.5 \times 10^7 \times 4.08 \times 10^{-5} \times [\text{O}]$$

$$[\text{O}] = 2.45 \times 10^{-4}$$

(ii) $\frac{d[\text{O}_2]}{dt} = 2r = 0.15 \times 2 = 0.3$



$$P_0 = 4 \text{ mm} \quad \quad \quad 0 \quad \quad 0 \quad \quad 0$$

$$P_t = (P_0 - x) \quad \quad \quad x \quad \quad x \quad \quad x$$

we know

$$P_t = P_0 e^{-Kt}$$

$$\frac{P_t}{P_0} = e^{-Kt}$$

$$\frac{P_t}{P_0} = e^{-(4.78 \times 10^{-3} \times 4.5 \times 60)}$$

$$\frac{P_t}{P_0} = e^{-1.29} = 0.275$$

Since composition is same therefore

$$\frac{r_2}{r_1} = \frac{P_2}{P_1} = 0.275 \quad \text{Ans.} \quad 0.275$$

47. Rate = $k[\text{B}][\text{A}]$

Rate = $k'[\text{A}]$

$$k' = k[\text{B}]$$

$$= 5 \times 10^{-3} \times 6$$

$$= 3 \times 10^{-2}$$

$$(C_t)_A = C_0 e^{-kt}$$

$$= 0.1 e^{-3 \times 10^{-2} \times 100}$$

$$= 0.1 e^{-3} = 0.005 \text{ min}$$

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.



The value of k (velocity constant) is always independent of the concentration of reactant and it is a function of temperature only.

3. $t_{1/2} = 4 \text{ hours} \quad n = \frac{T}{t_{1/2}} = \frac{24}{4} = 6; \quad N = N_0 \left(\frac{1}{2}\right)^N$

or, $N = 200 \times$

$$\left(\frac{1}{2}\right)^6 = 200 \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = 3.125 \text{ g.}$$

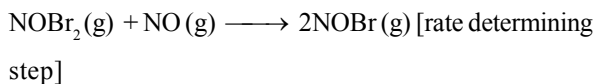
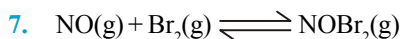
4. For endothermic reaction, $\Delta H = \text{ve}$

$$\Delta H = E_f - E_b, \text{ it means } E_b < E_f.$$

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 = $k[\text{CO}]^2$

Thus, according to the rate law expression doubling the concentration of CO increases the rate by a factor of 4.



$$\text{Rate of the reaction (r)} = k[\text{NOBr}_2][\text{NO}]$$

where $[\text{NOBr}_2] = K_c[\text{NO}][\text{Br}_2]$

$$r = k \cdot K_c \cdot [\text{NO}][\text{Br}_2][\text{NO}]$$

$$r = k'[\text{NO}]^2[\text{Br}_2]$$

The order of the reaction with respect to $\text{NO}(\text{g}) = 2$.

8. $\Delta H_R = E_f - E_b = 180 - 200 = -20 \text{ kJ mol}^{-1}$

The correct answer for this question should be -20 kJ 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.

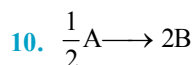
Given $A_0 = 10 \text{ A}$

$$A_0 \times N_0 \text{ and } A \times N$$

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N} = \frac{2.303}{\lambda} \log \frac{A_0}{A}$$

$$= \frac{2.303}{0.693} \log \frac{10A}{A} = \frac{2.303 \times 30}{0.693} \log 10 = \frac{2.303 \times 30}{0.693}$$

$$= 99.69 \text{ days} \approx 100 \text{ days.}$$



$$-\frac{1}{1/2} \frac{d(A)}{dt} = \frac{1}{2} \frac{d(B)}{dt}$$

$$\boxed{-\frac{d(A)}{dt} = \frac{1}{4} \frac{d(B)}{dt}}$$

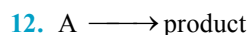
11. In first order reaction for X% completion

$$k = \frac{2.303}{t} \log \left(\frac{100}{100 - x\%} \right)$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \left(\frac{100}{100 - 99} \right)$$

$$= \frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$

So, $t = 46.06 \text{ min.}$



For zero order reaction

$$t_{1/2} \propto \frac{1}{a^{n-1}} \quad a = \text{initial concentration of reactant}$$

$$t_{1/2} \propto a$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_1}{a_2}; \quad \frac{1}{(t_{1/2})_2} = \frac{2}{0.50}$$

$$t_{1/2} = \frac{0.5}{2} = 0.25 \text{ h.}$$

13. Mechanism (1) rate = $K [Cl_2] [H_2S]$
 Mechanism (2) rate = $K_1 [Cl_2] [HS^-]$

$$K_{eq} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$[HS^-] = \frac{K_{eq}[H_2S]}{[H^+]}$$

$$= K_1 K_{eq} \frac{[Cl_2][H_2S]}{[H^+]}$$

\therefore Mechanism (1) is consistent with this rate equation.

14. $\frac{\text{Rate at } 50^\circ\text{C}}{\text{Rate at } T_1^\circ\text{C}} = (2)^{\frac{\Delta T}{T_1}} = (2)^{\frac{50}{10}} = 2^5$
 $= 32 \text{ times}$

15. $K_1 = A_1 e^{-E_{a1}/RT}$

$$K_2 = A_2 e^{-E_{a2}/RT}$$

$$\frac{K_1}{K_2} = \frac{A_1}{A_2} e^{(E_{a2} - E_{a1})/RT}$$

$$K_1 = K_2 A \times e^{E_{a1}/RT}$$

16. $K = \frac{1}{40} \ln \frac{0.1}{0.025} = \frac{1}{40} \ln 4$

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

$$= \frac{1}{40} \ln 4 (0.1) = \frac{2 \ln 2}{40} (0.1) = 3.47 \times 10^{-4}$$

17. $\log \frac{K_2}{K_1} = \frac{-E_a}{2.030R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

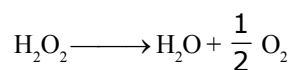
$$\frac{K_2}{K_1} = 2; \quad T_2 = 310 \text{ K} \quad T_1 = 300 \text{ K}$$

$$\Rightarrow \log 2 = \frac{-E_a}{2.303 \times 8.134} \left(\frac{1}{310} - \frac{1}{300} \right)$$

$$\Rightarrow E_a = 53598.6 \text{ J/mol} = 53.6 \text{ KJ/mol}$$

Ans is (1)

18. $k = \frac{1}{50} \ln \left(\frac{0.500}{0.125} \right) = \frac{1}{50} \cdot \ln(4) = \frac{2 \ln(2)}{50}$



$$POR = \frac{d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{1}{1/2} \frac{d[O_2]}{dt}$$

$$\frac{2}{50} \ln(2) \times 0.05 = 2 \cdot \frac{d[O_2]}{dt}$$

$$\frac{d[O_2]}{dt} = 0.693 \times 10^{-3} = 0.93 \times 10^{-4} \text{ mol/min}$$

19. From arrhenius equation

$$K = A.e^{\frac{-E_a}{RT}}$$

$$\text{so, } K_1 = A.e^{\frac{-E_{a1}}{RT}} \quad \dots\dots\dots (1)$$

$$K_2 = A.e^{\frac{-E_{a2}}{RT}} \quad \dots\dots\dots (2)$$

$$\text{so, equation (2)/(1)} \Rightarrow \frac{K_2}{K_1} = e^{\frac{(E_{a1}-E_{a2})}{RT}}$$

(As pre-exponential factors of both reactions is same)

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{E_{a1} - E_{a2}}{RT} = \frac{10,000}{8.314 \times 300} = 4$$

20. $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$

$r_1 = 1 \text{ torr sec}^{-1}$, when 5% reacted (95% unreacted)

$r_2 = 0.5 \text{ torr sec}^{-1}$, when 33% reacted (67% unreacted)

$r \propto (a-x)^m$ $m = \text{order of reaction}$

$a-x = \text{unreacted}$

$$\frac{r_1}{r_2} = \left[\frac{(a-x_1)}{(a-x_2)} \right]^m \Rightarrow \frac{1}{0.5} = \left(\frac{0.95}{0.67} \right)^m$$

$$2 = (1.41)^m \Rightarrow 2 = (\sqrt{2})^m \Rightarrow m=2$$

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

$$r = k[X] = \frac{0.693}{t_{1/2}} \times [X] = \frac{0.693}{20} \times 0.01$$

$$= 3.47 \times 10^{-4} \text{ M min}^{-1}.$$

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) $k = \frac{R_0}{[A_0]} = \frac{0.05}{0.10} = 0.5 \text{ sec}^{-1}.$

3. $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

$$t = 0 \quad 800 \quad - \quad -$$

$$t \quad 800-2x \quad 3x \quad 2x = (800+3x)$$

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 P_x decreases from 400 to 200 to again $t_{1/2} = 100$ min. Since half left is independent of initial concentration so reaction must be 1st order with respect to X.

$$\text{Rate constant } K = \frac{\ln 2}{t_{1/2}} = 6.93 \times 10^{-3} \text{ min}^{-1}.$$

Time taken for 75% completion = $2 \times t_{1/2} = 200$ min.

Now when $P_x = 700 = 800 - 2x$ 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. $aG + bH \longrightarrow \text{products}$

$$\text{Rate} = k[G]^x[H]^y$$

$$R = K [G]_0^x [H]_0^y \quad (\text{Let initial conc. are } [G]_0 \text{ \& } [H]_0)$$

$$8R = K[2G]_0^x [2H]_0^y = K2^{x+y}R$$

$$\text{so } 2^{x+y} = 8 \Rightarrow x+y=3$$

8. For 1st order reaction

For zero order reaction

$$k_1 = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{40} \text{ second}^{-1}$$

$$k_0 = \frac{C_0}{2 t_{1/2}} = \frac{1.386}{2 \times 20} \Rightarrow \frac{k_1}{k_0} = \frac{0.693}{1.386} = 0.5.$$

9. From Arrhenius equation

$$K = Ae^{-E_a/RT}$$

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

$$2.303 \log K = 2.303 \log A - \frac{E_a}{RT}$$

$$\log K = \frac{-E_a}{2.303R} \times \frac{1}{T} + \log A \quad \dots\dots (A)$$

$$\log K = -(2000) \frac{1}{T} + 6 \quad \dots\dots (B)$$

On comparing equation (A) and (B)

$$\frac{-E_a}{2.303R} = -2000.$$

$$E_a = 2.303 \times 8.314 \times 2000 = 38.29 \text{ kJ and } \log A = 6$$

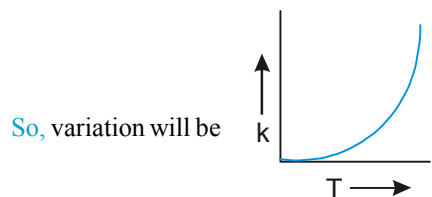
$$A = 10^6$$

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. $k = Ae^{-E_a/RT}$



12.* $C_t = C_0 e^{-Kt}$

$$t_{1/2} \propto \frac{1}{K}, \quad K \uparrow \text{ on increasing } T.$$

After eight half lives,

$$C = \frac{C_0}{2^8}$$

$$\Rightarrow \% \text{ completion} = \frac{C_0 - \frac{C_0}{2^8}}{C_0} \times 100 = 99.6\%$$

13. $Kt_{1/8} = \ln \left\{ \frac{C_0}{C_0/8} \right\} = \ln 8$

$$Kt_{1/10} = \ln \left\{ \frac{C_0}{C_0/10} \right\} = \ln 10$$

$$\text{then } \frac{t_{1/8}}{t_{1/10}} \times 10 = \frac{\ln 8}{\ln 10} \times 10 = \frac{\log 2}{\log 10} \times 10 = 9$$

14. For P, if $t_{50\%} = x$

$$\text{then } t_{75\%} = 2x$$

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 $0 + 1 = 1 \rightarrow$ Ans. is D

15. A high activation energy usually implies a slow reaction.

16. Steric factor(P) = $\frac{(A/Z)_{\text{exp}}}{(A/Z)_{\text{theo}}}$

A = frea.factor

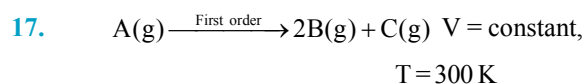
Z = Collision freq.

usually $P < 1$

$\therefore A_{\text{exp}} < A_{\text{theo}}$. Assuming 'Z' to be same

Here $P > 1$

$$\therefore A_{\text{exp}} > A_{\text{theo}}$$



$$t = 0 \quad P_0$$

$$t = t_{1/3} \quad \left(P_0 - \frac{2P_0}{3} \right) \quad \frac{4P_0}{3} \quad \frac{2P_0}{3}$$

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

$$t = t \quad P_0 - x \quad 2x \quad x$$

$$\text{So, } P_t = P_0 - x + 2x + x = P_0 + 2x$$

$$\text{or } 2x = P_t - P_0$$

$$t = \frac{1}{k} \ln \frac{P_0}{(P_0 - x)}$$

$$\text{or } t = \frac{1}{k} \ln \frac{P_0}{P_0 - \frac{(P_t - P_0)}{2}} = \frac{1}{k} \ln \frac{2P_0}{2P_0 - P_t + P_0}$$

$$\text{or } Kt = \ln \frac{2P_0}{3P_0 - P_t}, Kt = \ln 2P_0 - \ln(3P_0 - P_t)$$

$$\text{or } \ln(3P_0 - P_t) = -Kt + \ln 2P_0$$

Graph between $\ln(3P_0 - P_t)$ vs 't' is a straight line with negative slope.

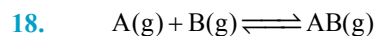
So (A) is correct option.

$$t_{1/3} = \frac{1}{K} \ln \frac{P_0}{(P_0/3)} = \frac{1}{K} \ln 3 \Rightarrow \text{It is independent of initial concentration.}$$

So (B) is wrong option.

As rate constant is a constant quantity and independent of initial concentration.

So Graph (D) is correct.



$$E_{a_b} = E_{a_f} + 2RT \quad \& \quad A_f = 4 A_b$$

Now, Rate constant of forward reaction

$$k_f = A_f e^{-E_{a_f}/RT}$$

$$\text{Rate constant of reverse reaction } K_b = A_b e^{-E_{a_b}/RT}$$

Equilibrium constant

$$K_{eq} = \frac{K_f}{K_b} = \frac{A_f}{A_b} e^{-(E_{a_f} - E_{a_b})/RT}$$

$$= 4e^{+2} = 4e^2$$

$$\begin{aligned} \text{Now, } \Delta G^\circ &= -RT \ln K_{eq} = -2500 \ln(4e^2) \\ &= -2500 (\ln 4 + \ln e^2) \\ &= -2500 (1.4 + 2) = -2500 \times 3.4 \\ &= -8500 \text{ J/mole} \end{aligned}$$

MOCK TEST

1. (C)

2. (C)

3. (C)

As only A is optically active. So conc. of A at $t = 20$ min $\propto 30^\circ$

While concentration of A at $t = 50$ min $\propto 15^\circ$

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)

$$\text{So volume consumed} = (30 \text{ ml}) + \left(\frac{30}{2} \text{ ml}\right) + \left(\frac{30}{4} \text{ ml}\right)$$

= 52.5 ml ans.

4. (B)

$$r_2 = k_2 [A]_2^1 [B]_2^1 \quad \text{for a certain run}$$

$$r_1 = k_1 [A]_1^1 [B]_1^1 \quad \text{for a previous run}$$

dividing, we get

$$\frac{r_2}{r_1} = \frac{k_2 [A]_2 [B]_2}{k_1 [A]_1 [B]_1}$$

Substituting the given information

$$1.5 = 2^{\left(\frac{t_2 - 27}{10}\right)} \times \frac{1}{2} \times \frac{1}{2}$$

$$\Rightarrow 6 = 2^{\left(\frac{t_2 - 27}{10}\right)} \Rightarrow \frac{t_2 - 27}{10} \ell n 2 = \ell n 6$$

$$\Rightarrow \frac{t_2 - 27}{10} = \frac{\ell n 6}{\ell n 2} \Rightarrow t_2 = 52.85^\circ\text{C} \approx 53^\circ\text{C}$$

5. (C)

$$\frac{[B]}{[C]} = \frac{3k_1}{8k_1} = \frac{3}{8} = \alpha$$

$$\frac{[C]}{[D]} = \frac{8k_2}{7.5k_2} = \frac{8}{7.5} = \beta$$

$$\therefore \alpha\beta = 0.4$$

6. (C)

$t_{1/2} = K a^{(1-n)}$, n being order = Rate constant

$$\log t_{1/2} = \log K + (1-n) \log a$$

$$1 - n = -1$$

$$n = 2$$

7. (D)

$$\text{Rate (SN}^2\text{)} = 5.0 \times 10^{-5} \times 10^{-2} [R-X] = 5.0 \times 10^{-7} [R-X]$$

$$\text{Rate (SN}^1\text{)} = 0.20 \times 10^{-5} [R-X]$$

$$\% \text{ of SN}^2 = \frac{5 \times 10^{-7} [R-X] \times 100}{5 \times 10^{-7} [R-X] + 0.20 \times 10^{-5} [R-X]} = 20$$

8. (D)

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

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

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

$$\text{Comparision indicates } \frac{\ln(TC)}{10} = \frac{\ln 3}{10}$$

$$\Rightarrow TC = 3$$

9. (C)

$$k = -2.303 (\text{slope}) \text{ min}^{-1} = -2.303 (-0.03) \text{ min}^{-1} = 0.06909 \text{ min}^{-1} = 4.14 \text{ hr}^{-1} \approx 4 \text{ hr}^{-1}$$

10. (A)

$$\frac{n_{CH_4} + n_{CO_2}}{n_{CH_2CO} + n_{H_2O}} = \frac{k_1}{k_2}$$

$$\Rightarrow \frac{n_{CH_4} + n_{CO_2}}{n_{CH_4} + n_{CO_2} + n_{CH_2CO} + n_{H_2O}} = \frac{k_1}{k_1 + k_2}$$

$$\Rightarrow \frac{2n_{CH_4}}{n_{total}} = \frac{k_1}{(k_1 + k_2)}$$

$$\Rightarrow \frac{n_{CH_4}}{n_{total}} = \frac{k_1}{2(k_1 + k_2)}$$

$$\Rightarrow \frac{n_{CH_4}}{n_{total}} \times 100 = \frac{50k_1}{(k_1 + k_2)}$$

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.

$$\text{so rate} = k [\text{sugar}]^1 [\text{H}^+]^n$$

[n = order w.r.t. H^+ ion]

$$\text{Also } t_{1/2} \text{ for } [\text{H}^+] \propto \frac{1}{[\text{C}_0]^{n-1}} \text{ or } \propto \text{C}_0^{1-n}$$

$$\therefore 600 \propto [10^{-5}]^{1-n}$$

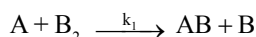
$$60 \propto [10^{-6}]^{1-n}$$

$$\text{or } 10 = (10)^{1-n} \quad \text{or} \quad 1 - n = 1$$

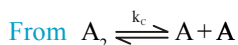
$$n = 0$$

12. (C)

Rate is governed by slowest step



$$r = k_1 [\text{A}] [\text{B}_2] \quad \text{.....(i)}$$



$$k_c = \frac{[\text{A}]^2}{[\text{A}_2]} \quad \text{.....(ii)}$$

$$[\text{A}] = \sqrt{k_c} [\text{A}_2]^{1/2}$$

$$r = k_1 \sqrt{k_c} [\text{A}_2]^{1/2} [\text{B}_2] \quad \text{order is} = \frac{1}{2} + 1 = \frac{3}{2}$$

13. (A)

14. (B)

rate is slope of curve

$$\text{at 20 sec } \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.35}{50} \quad (\text{approx})$$

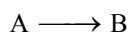
$$= 7 \times 10^{-3} \text{ M sec}^{-1}$$

at 40 sec rate become half because of first order

$$r_{40\text{sec}} = 3.5 \times 10^{-3} \text{ M sec}^{-1}$$

$$r_{60\text{sec}} = 1.75 \times 10^{-3} \text{ M sec}^{-1}$$

$$r_{80\text{sec}} = \frac{1.75}{2} \times 10^{-3}$$



$$t = 00.4$$

$$t = 60 \quad \begin{array}{cc} 0.4 - x & x \\ = 0.05 & 50 \end{array} \quad x = 0.35$$

15. (B C)

16. (A B D)

17. (A B D)

$$\begin{array}{ccc} 0 & 30 & x \\ 30 & 20 & -15 \end{array}$$

$$k = \frac{1}{30} 2.3 \log \frac{45}{35}$$

$$\therefore t_{1/2} = 75 \text{ min}$$

$$k = \frac{1}{t} 2.3 \log \frac{45}{0 - (-15)}$$

$$t = 120 \text{ min}$$

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

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

$$\Rightarrow x = 22.5 - 15 = 7.5^\circ$$

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 $K = A e^{-E_a/RT}$ when $E_a = 0$, $K = A$.

21. (C)

22. (B)

It is fact

23. (B)

$$\log K_b = \log A - \frac{E_a}{2.303RT}$$

$$\log K_b = 12 - \frac{57450}{2.303 \times 8.314 \times 300}$$

$$\log K_b = 2$$

$$K_b = \text{Antilog } 2$$

$$K_b = 10^2$$

$$K_c = \frac{K_F}{K_b} \Rightarrow 10^4 = \frac{K_F}{10^2} \Rightarrow K_F = 10^6$$

24. (A)

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = 20 - T \times 0.07$$

 For non-spontaneous process $\Delta G > 0$

$$\text{hence } 0 < 20 - T \times 0.07$$

$$T < \frac{20}{0.07} \Rightarrow T < 285.7 \text{ K}$$

25. (C)

$$K_p = K_c (RT)^{\Delta n}$$

$$= 10^4 (0.082 \times 300)^1$$

$$= 24.6 \times 10^4$$

26. (A)

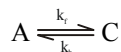
$$-\frac{dA}{dt} = k_f[A] - k_b[C]$$

$$\text{and } \frac{d[C]}{dt} = k_f[A] - k_b[C] \text{ at any time}$$

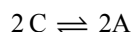
and slope between conce and time is known as rate and they are always equal at any time.

27. (D)

28. (D)



$$K_c = \frac{k_f}{k_b} = \frac{[C]}{[A]} = \frac{0.4}{0.6} = \frac{2}{3} \text{ from graph}$$



$$K'_c = \left(\frac{1}{K_c} \right)^2 = \left(\frac{3}{2} \right)^2 = \frac{9}{4}$$

29. (A)

$$[A]_t = 1 \times e^{-kt} = e^{-3 \times 33.33 \times 10^{-2}} = e^{-0.999} = \frac{1}{e}$$

30. (C)



$$2Z + 3Z = b \Rightarrow 5Z = b$$

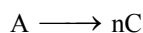
$$(Z-x) + 2x + 3x = a$$

$$\Rightarrow Z + 4x = a$$

$$4Z - 4x = b - a \quad (Z-x) = \frac{b-a}{4}$$

$$k = \frac{1}{t} \ln \left(\frac{\frac{b}{5}}{\frac{b-a}{4}} \right)$$

31. (A)



$$[A]_0 - \frac{7[A]_0}{8} = \frac{7[A]_0}{8}n \Rightarrow \frac{[A]_0}{8} = \frac{7[A]_0}{8}n$$

$$\Rightarrow n = \frac{1}{7} \quad \text{or} \quad \frac{1}{n} = 7.$$

 32. (A \rightarrow p, r); (B \rightarrow p, r, s); (C \rightarrow q); (D \rightarrow p, r, s)

(A) IInd order reaction

(B) & (D) Ist order reaction

(C) zero order reaction

 33. (A \rightarrow p, q); (B \rightarrow p, r, s); (C \rightarrow s); (D \rightarrow p, q)

 34. (A \rightarrow q), (B \rightarrow s), (C \rightarrow r), (D \rightarrow p)

 35. Arrhenius equation $k = Ae^{-E_a/RT}$

$$\text{or } \log_{10} k = \log A - \frac{E_a}{2.303RT}$$

Comparing the given equation with equation (i),

$$\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4 (K)}{T}$$

$$\Rightarrow E_a = 2.303 \times 1.25 \times 10^4 \times 8.3 = 238936.25 \text{ J mol}^{-1}$$

$$k = \text{antilog} \left[12.37 - \frac{1.25 \times 10^4}{750} \right] = \text{antilog} (-4.3) \text{ sec}^{-1}$$

$$= 5 \times 10^{-5} \text{ sec}^{-1}$$

$$\therefore E_{ak} = 238936.25 \times 5 \times 10^{-5} = 11.95 \Rightarrow 12$$

Hence Ans. 12

36. t :	0	5	15	35
[A] :	1	0.5	0.25	0.125

IInd order of the reaction

Ans. 2

$$37. \frac{dx(1+bx)}{(a-x)} = Kdt$$

$$dx \frac{[1 - b(a-x) + ab]}{(a-x)} = Kdt$$

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

$$-(1+ab) \log(a-x) - bx = Kt - (1+ab) \log a$$

$$Kt = (1+ab) \log \frac{a}{(a-x)} - bx$$

$$\text{at } t = t_{1/2} \quad x = \frac{a}{2}$$

$$K_{1/2} = (1 + ab) \log \frac{a}{a - \frac{a}{2}} - \frac{b \cdot a}{2} = (1 + ab) \log 2 - \frac{ba}{2}$$

$$= \log 2 + ab \log 2 - ba \times 0.5$$

$$t_{1/2} = \frac{\log 2 + ab(\log 2 - 0.5)}{K}$$

38. (a) It is obvious 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 = $\eta = (\text{constant}) e^{-\frac{E_a}{RT}}$

$$\therefore \ln \eta = \ln (\text{constant}) - \frac{E_a}{RT}$$

$$\frac{d \ln \eta}{dT} = \frac{E_a}{RT^2}, \quad \frac{1}{\eta} \frac{d\eta}{dT} = \frac{E_a}{RT^2}$$

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} .

$$\therefore 0.02 = \frac{E_a}{1.987 \times (298)^2}$$

$$E_a = 0.02 \times 1.987 \times (298)^2 \text{ cal/mol}$$

$$E_a = 3529 \text{ cal mol}^{-1}$$

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