

### Exercise - 1 (A)

$$1. \quad -\frac{1}{2} \frac{d\{SO_2\}}{dt} = \frac{1}{2} \frac{d\{SO_3\}}{dt} \Rightarrow \frac{d\{SO_2\}}{dt} = \frac{100}{80} \times 64 \text{ kg/min}$$

$$2. \quad N_2 + 3H_2 \rightarrow 2NH_3 \quad -\frac{1}{3} \frac{d\{H_2\}}{dt} = \frac{1}{2} \frac{d\{NH_3\}}{dt} \Rightarrow -\frac{d\{H_2\}}{dt} = \frac{3}{2} \times 40 \times 10^{-3}$$

$$3. \quad \text{rate} = -\frac{d\{A\}}{dt} = -\frac{1}{2} \frac{d\{B\}}{dt}$$

4. relative strength  $\propto$  rate constant

$$5. \quad \text{For } xA + yB \rightarrow zC \quad -\frac{1}{x} \frac{d\{A\}}{dt} = -\frac{1}{y} \frac{d\{B\}}{dt} = \frac{1}{z} \frac{d\{C\}}{dt}$$

$$6. \quad PV = nRT \Rightarrow \frac{n}{v} = \frac{P}{RT} \Rightarrow C = \frac{n}{v} = \frac{P}{RT} \Rightarrow \frac{dC}{dt} = \frac{1}{v} \left( \frac{dn}{dt} \right) = \frac{1}{RT} \left( \frac{dP}{dt} \right)$$

$$7. \quad -\frac{1}{2} \frac{d\{NH_3\}}{dt} = \frac{d\{N_2\}}{dt} = \frac{1}{3} \frac{d\{H_2\}}{dt} \Rightarrow K_{\frac{1}{2}} = K_2 = K_{\frac{3}{3}} \Rightarrow 1.5K_1 = 3K_2 = K_3$$

$$8. \quad \text{rate} = k\{A_0\} = 60 \times 10^{-4} \times 0.01 \text{ M sec}^{-1}$$

$$9. \quad \text{conc.} \propto \frac{1}{V} \quad \text{so rate} \propto \frac{1}{V^3}$$

$$10. \quad \text{rate} = k\{N_2O_5\}$$

$$11. \quad -\frac{d\{N_2O_5\}}{dt} = \frac{1}{2} \frac{d\{NO_2\}}{dt} = 2 \frac{d\{O_2\}}{dt}$$

$$12. \quad \text{rate} = \frac{1}{2} \frac{\{A\}_t - \{A\}_0}{t} = \frac{1}{2} \frac{0.5 - 0.4}{10} = 0.005 \text{ M min}^{-1}$$

$$13. \quad t_{1/2} \propto \frac{1}{a_0^{n-1}} \Rightarrow n - 1 = 2 \Rightarrow n = 3$$

14. as per theory

$$15. \quad \text{rate} = k\{A\}\{B\} \text{ i.e. rate} \propto n_A n_B$$

16. rate constant is independent of number of moles

17. rate is independent of concentration of reactants

$$18. \quad \text{as } -\frac{1}{2} \frac{d\{A\}}{dt} = \frac{d\{B\}}{dt} = \text{rate, so order w.r.t A is 2}$$

$$19. \quad K = \frac{\text{rate}}{\{A\}\{B\}^2} = \frac{10^{-2}}{1}, \quad \text{rate} = 10^{-2} \times (0.5)(0.5)^2 = 1.25 \times 10^{-3} \text{ Ms}^{-1}$$

20. rate  $\propto \{A\}^2 \{B\}^3$

21. Concentration [A] effectively unchanged so rate  $\propto [B]$

Pseudo-unimolecular

22.  $K = \frac{\text{rate}}{\{C\}^3} = \text{lit}^2 \text{mol}^{-2} \text{min}^{-1}$

23. as question number 22

24.  $K = \frac{2.303}{t} \log \frac{\{A_0\}}{\{A_t\}} \quad \{A_t\} = \frac{\{A_0\}}{2}, \quad \text{rate} = k \frac{\{A_0\}}{2}$

25.  $t_{1/2} \propto a_0^{1-n}$  as  $n = \frac{1}{2}$

$$\frac{\left(\frac{t_{1/2}}{2}\right)_1}{\left(\frac{t_{1/2}}{2}\right)_2} = \left(\frac{A_0}{\frac{A_0}{2}}\right)^{1/2} = 2^{1/2} \Rightarrow \left(\frac{t_{1/2}}{2}\right)_1 = \frac{(t_{1/2})_1}{\sqrt{2}} = 11.3$$

$$t_{75\%} = \left(\frac{t_{1/2}}{2}\right)_1 + (t_{1/2})_2 = 27.3 \text{ min}$$

26.  $t_{1/2}$  will be 4 hrs

So it will take 4 hrs to become from 0.6 to 0.3 M

27.  $\{A_0\} \propto V_\infty, \{A_t\} \propto V_\infty - V_t$

28.  $-\frac{d\{A\}}{dt} = k\{A\}^{1/3} \Rightarrow -\int_{A^0}^{A_0/2} \frac{d\{A\}}{\{A\}^{1/3}} = \int_0^{t_{1/2}} dt$

$$\Rightarrow \frac{3}{2} \left[ \{A_0\}^{2/3} - \left\{\frac{A_0}{2}\right\}^{2/3} \right] = kt_{1/2} \Rightarrow t_{1/2} = \frac{\frac{3}{2} \{A_0\}^{2/3} (2^{2/3} - 1)}{2^{2/3} K}$$

29.  $\frac{dx}{dt} = k \Rightarrow x = kt$  &  $x = kt$  &  $t_{1/2} \propto \{A_0\}$

30.  $k = \text{rate} = \text{conc. time}^{-1}$

31. As reaction is zeroth order, rate = constant

$$\text{rate} = -\frac{18 - 20}{10 - 5} = 0.4 \text{ mol / min}$$

32. As per theory

33.  $K = \frac{2.303}{90} \log \left( \frac{10}{10-9} \right) \quad t_{1/2} = \frac{0.693}{k} = 27 \text{ min}$

$$34. \quad \text{As } kt = 2.303 \log \left( \frac{a}{a-x} \right)$$

$$kt = 2.303 (\log a - \log(a-x)) \quad \& \quad t_{\frac{1}{2}} = \frac{0.693}{k} = \text{constant}$$

$$35. \quad \{A_0\} \text{ after 2 half life} = \frac{10}{2^2} = 2.5$$

$$36. \quad (t_{1/2})_{\text{zeroth}} = \frac{\{A_0\}}{2k_0} \dots(1) \qquad (t_{1/2})_{1st} = \frac{0.693}{k_1} \dots(2)$$

$$\frac{\{A_0\}}{2k_0} = \frac{0.693}{k_0}$$

$$\frac{(\text{rate})_{1st}}{(\text{rate})_{0th}} = \frac{k_1 \{A_0\}}{k_0} = 2 \times 0.693$$

$$37. \quad \frac{dx}{dt} = k \{A\}^3 = k(a-x)^3$$

$$\int_0^x \frac{dx}{(a-x)^3} = \int_0^y k dt$$

$$\Rightarrow \left[ \frac{1}{2(a-x)^2} - \frac{1}{2a^2} \right] = kt$$

$$38. \quad \text{at } t = t_{1/2}$$

$$\Rightarrow x = \frac{a}{2}$$

$$\text{so } T_{1/2} = \frac{3}{2ka^2}$$

$$39. \quad \text{rate} = -\frac{1}{2} \frac{d\{NO\}}{dt} = k\{NO\}^2[O_2] \Rightarrow -\frac{d\{NO\}}{dt} = K'\{NO\}^2[O_2]$$

$$\text{rate} = -\frac{d\{NO\}}{2dt} = -\frac{d\{O_2\}}{dt} = \frac{d\{NO_2\}}{2dt}$$

$$40. \quad x = a(1 - e^{-kt}) \Rightarrow a - x = ae^{-kt}$$

$$\text{at } t = \frac{1}{k} \quad a - x = \frac{a}{e}$$

$$a - x = ae^{-kt}$$

$$41. \quad \text{at } t = \frac{2}{k}, \quad a - x = \frac{a}{e^2}$$

42.  $\log T_{50}$  is independent on  $\log a$  hence 1<sup>st</sup> order reaction.

$$43. k = \frac{2.303}{t} \log \left( \frac{a}{a-x} \right) = \frac{(2.303 \times \log 8)}{10} = \frac{2.303 \times 3 \log 2}{10}$$

44. Unit of rate constant for 1<sup>st</sup> order is  $\text{sec}^{-1}$

$$x = kt$$

$$45. \Rightarrow a - x = 0.5 \Rightarrow a - 2 \times 25 \times 10^{-2} = 0.5$$

$$a = 1.0 \text{ M}$$

$$46. k = \frac{\text{rate}}{\{\text{conc}\}} = 1.5 \times 10^{-3} \text{ s}^{-1}$$

$$47. 100\% \xrightarrow{1/2 \text{ hours}} 50\% \xrightarrow{1/2 \text{ hours}} 25\%$$

$$48. A \rightarrow B \Rightarrow \{A\} = \{B\} = \frac{\{A_0\}}{2}, t = t_{1/2}$$

$$49. T_{50} \text{ is independent of conc. for 1}^{\text{st}} \text{ order kinetic, } \log T_{50} = \log \left( \frac{0.69}{k} \right) = \text{constant} = \text{parallel to x-axis}$$

50.  $x = kt$  for straight line & positive slope hence zeroth order reaction.

51. As  $t_{1/2}$  is constant

$$0.2 \xrightarrow{5 \text{ hours}} 0.1 \xrightarrow{5 \text{ hours}} 0.05$$

52. As per theory

53. for  $\text{rate} \propto \{B\}$

$$\text{so rate} \propto \{A\}^2$$

(as  $A \rightarrow 2A$  &  $B \rightarrow 2B$  rate  $\rightarrow 8$  times)

54. As per derivation

55. As  $t_{1/2}$  is independent on sugar concentration &  $t_{1/2} \propto \{H^+\} \text{ so } r = k \{sugar\}^1 \{H^+\}^0$

56.  $\text{rate} \propto \{A\} \{B\}^0 \{C\}^2$ , order = 2 + 1

$$57. kt = 2.303 \left( \log P_{N_2O_5}^0 - \log P_{N_2O_5} \right)$$

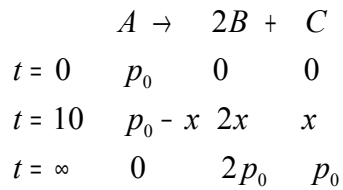
58. rate is independent on conc.

$$k = \text{rate} = \frac{0.069 - 0.052}{17 - 0} = 0.001 \text{ M min}^{-1}$$

59.  $\text{rate} \propto \{A\}, \text{rate} \propto \{B\}^0 \text{ rate} = k\{A\}$

60.  $\log\{A_0\}_0 - \log\{A\}_t = \frac{k}{2.303}t$

61.



at  $3P_0 = 270 \Rightarrow P_0 = 90 \text{ mm of Hg}$   $t = 10$   $P_0 + 2x = 176 \Rightarrow x = 43$

So  $p_0 - x = 90 - 43 = 47 \text{ mm}$

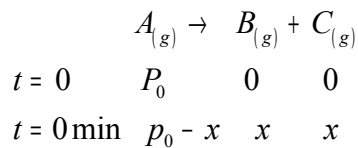
62. As per theory

63. As per theory

64.  $\frac{r_\infty - r_0}{2} = r_\infty - r_t$  as  $\frac{a}{2} = a - x$

65. As per theory

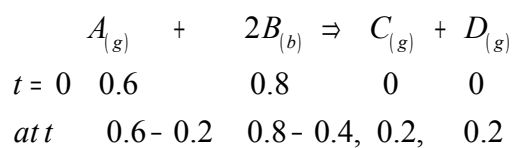
66.



$p_0 - x = 120$   $x = 20 \text{ mm}$

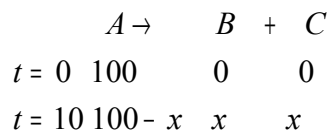
$$k = \frac{2.303}{10} \log\left(\frac{P_0}{r_0 - x}\right)$$

67.



$$\frac{(\text{rate})_t}{(\text{rate})_{t_0}} = \frac{(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{64}{6 \times 64} = \frac{1}{6}$$

68.



$$100 + x = 120 \quad x = 20$$

$$k = \frac{2.303}{10} \log \left( \frac{100}{100 - 20} \right)$$

69. As per theory

70.  $\frac{d\{B\}}{dt} = k\{A\}$  rate of formation -  $k_2\{B\}$  rate of disappear into C

71. By diffraction  $\frac{d\{x\}}{dt} = k_1(a - x) - k_2(a - x)$

72.  $\frac{\{B\}}{\{C\}} = \frac{k_1}{k_2} = 0.33 \Rightarrow \{B\} + \{C\} = 1.33\{C\} \quad \frac{\{B\}}{\{B\} + \{C\}} = \frac{0.33}{1.33} = 24.8\%$

73.  $\frac{k_1}{k_2} = 2 \times 10^9 \text{ C}^2 \text{ mol}^{-2}$

74. As per theory

75. 1<sup>st</sup> reaction is slow i.e r. d.s

76. As  $\frac{dx}{dt} = 0$

77. X is intermediate complex

78.  $k = Ae^{-Ea/Rt}$  at  $T \rightarrow \infty \quad k = A$

79.  $\log k = \log A - \frac{Ea/Rt}{2.303}$

80.  $K = Ae^{-Ea/RT} \quad k \propto e^{-Ea} \propto \frac{1}{e^{Ea}}$

81. as  $k \propto \frac{1}{e^{Ea}}$

83. As per theory

$$84. \quad \frac{E_a}{2.303RT} = \frac{2000}{T} \Rightarrow E_a \approx 9.16 \text{ kcal}$$

85. For exothermic  $r \times n$

$$E_{a_f} - E_{a_b} = -200 \text{ kJ} \quad E_{a_b} = 280 \text{ kJ}$$

$$86. \quad E_{a_f} - E_{a_b} = -20 \text{ kJ}$$

$$87. \quad E_{a_f} - E_{a_b} = -30$$

$$88. \quad E_{a_f} - E_{a_b} = -10$$

$$89. \quad x - E_{a_b} = y \Rightarrow E_{a_b} = x - y$$

$$90. \quad 2.303 \log(k_2/k_1) = \frac{E_a}{k} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

$$91. \quad \log k = \log A - \frac{E_a}{2.303RT}$$

$$\text{Slope} = - \frac{E_a}{2.303R} = \frac{1}{2.303} \Rightarrow E_a = R$$

92. as in (ii) order w.r.t  $H_2$  &  $ICl$  both are 1 in slow step

93. as rate  $\propto [A][B]$  so  $A + B \Rightarrow AB$  will be r.d.s

95. As II & IV are having high P.E. so highly unstable & they represent transition state

96. As, A & BC are reactants & AC is intermediate

$$97. \quad \frac{k_1}{k_2} = e^{-\frac{(E_{a1} - E_{a2})}{RT}} = e^{\frac{1000}{300}} = 28$$

98. rate is given by slow step

$$99. \quad \{O_2\}\{O\} = k_{eq}\{O_3\} \Rightarrow \{O\} = k_{eq} \frac{\{O_3\}}{\{O_2\}} \text{ rate} \propto \{O\}\{O_3\} \propto \frac{\{O_3\}^2}{\{O_2\}}$$

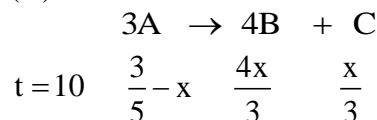
100.  $A \rightarrow B$  as  $K_1$  is small

101.  $rate = k\{x_2\}$  (as its slow step) order = 1

## EXERCISE - 1 [B]

1. (B)

2. (A)



$$P = 1 = \frac{3}{5} + \frac{2x}{3} \Rightarrow x = \frac{3}{5}$$

$$\frac{-d[A]}{dt} = \frac{3}{10} \text{ atm/min}^{-1}$$

3. (D)

$$r = k[G][H]^2.$$

4. (D)

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

$$\Rightarrow 0.1 = k \times 0.5^2 \times 2$$

$$\Rightarrow r = k \times 2^2 \times 3$$

5. (C)

$$k_1 t = \ln\left(\frac{1}{a}\right)$$

$$k_2 (2t) = \ln\left(\frac{1}{a^2}\right)$$

:

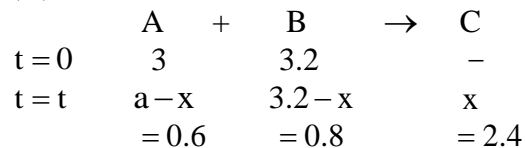
$$k_1 = k_2 = \dots\dots$$

$\Rightarrow$  1<sup>st</sup> order reaction

6. (C)

$$Kt \Rightarrow \frac{7a}{8} = \frac{a}{200} \times t \Rightarrow t = 175 \text{ sec}$$

7. (A)

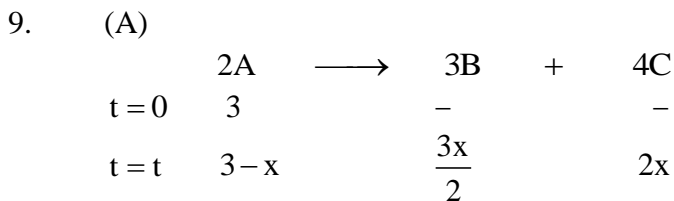


$$t = \frac{-1}{k(b-a)} \ln\left[\left(\frac{b}{b-x}\right) \times \frac{(a-x)}{a}\right]$$

$$= \frac{-1}{10^{-2} \times 0.2} \ln\left(\frac{3.2}{0.8} \times \frac{9.6}{3}\right) = \frac{1}{2 \times 10^{-3}} \ln\left(\frac{5}{4}\right)$$



8. (B)  
 $[A]_t = 0.3 - 10^{-2} \times 10 = 0.2M$   
 Zero order reaction



$$P_T = 3 + \frac{5x}{2}$$

At t = 10 min, x = 1.5

At t = 20 min, x = 3.0

Rx<sup>n</sup> goes to completion and follows  $x = kt$

10. (C)

11. (D)  
 $E_{af} - E_{ab} = \Delta H \Rightarrow E_{ab} = 120 \text{ kJ}$

After addition of catalyst.

$$E_{ab} = 120 - 60 = 60 \text{ kJ}$$

$$\text{Ration} = \frac{120}{60} = \frac{2}{1}$$

12. (D)

13. (A)

$$\ln k = 30 - \frac{40}{T} + 20T^2 - 30 \ln T$$

$$\frac{d(\ln k)}{dT} = +\frac{40}{T^2} + 40T - \frac{30}{T} = \frac{E_a}{RT^2}$$

$$\Rightarrow E_a = R [40 + 40T^3 - 30T]$$

$$\text{At } T = 300\text{K}, E_a \approx 1.08 \times 10^9 \text{ R}$$

14. (D)

15. (D)

## EXERCISE - 1 [C]

1. (2000)

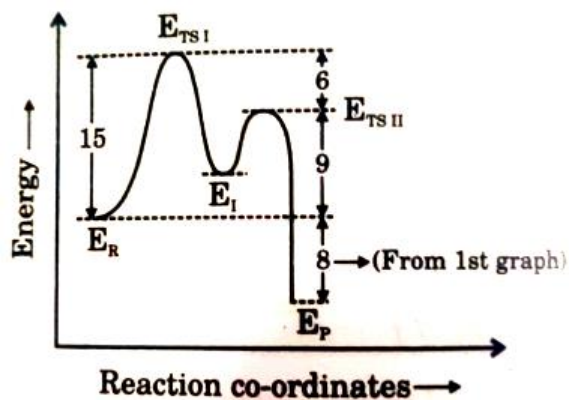
$$k_1 = k_2$$

$$\Rightarrow 10^{11} e^{-\frac{43.10}{RT}} = 10^{12} e^{-\frac{81.28}{RT}}$$

$$\Rightarrow -\frac{43.10}{RT} \times 10^3 = 2.3 - \frac{81.28}{RT} \times 10^3$$

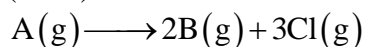
$$\Rightarrow T = \frac{38.18 \times 10^3}{2.3 \times 8.3} \text{ K}$$

2. (17)



$$\therefore E_{TS II} - E_P = 17 \text{ kJ/mol}$$

3. (2571)



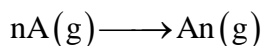
$$\begin{array}{ccc} 500 & - & - \\ 500 - P & 2P & 3P \end{array}$$

$$k \times 90 = \ln \left( \frac{2100 - 500}{2100 - 1900} \right)$$

$$k = \frac{3 \times 0.7}{90 \times 60} \text{ sec}^{-1}$$

$$t_{av} = \frac{1}{k} = \frac{30 \times 60}{0.7} = 257.18$$

4. (5)



$$t = 0 \quad 2 \quad -$$

$$t = t \quad 2 - x \quad \frac{x}{n}$$

$$2 - x + \frac{x}{n} = 1.2 \quad ; \text{ put } x = 1 (t_{1/2} = 20 \text{ min})$$

$$\Rightarrow n = 5$$

5. (2)

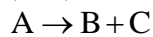
$$2 \times 10^{-2} \times 1 \times 100 = 2 \text{kJ}$$

6. (12)

$$\frac{d[\text{C}]}{dt} = 4 \times 10^{-3} \times 10^{-3} = 4 \times 10^{-6} \text{M} / \text{min}$$

$$\Rightarrow 4 \times 10^{-6} \times 1 \times 10 \times 30 \times 10^3 \text{cal} / \text{min} = 1.2 \text{cal} / \text{min}$$

7. (420)



$$k \times \frac{10}{60} = \ln \left[ \frac{10+10}{0+10} \right]$$

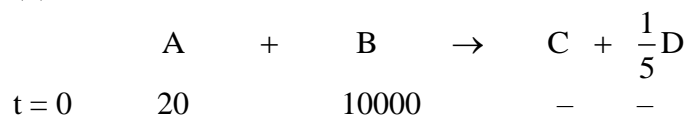
$$\Rightarrow k = 4.2 \text{hr}^{-1}$$

8. (2)

$$\frac{120}{15} = (\mu) \frac{(55-25)}{10}$$

$$\Rightarrow \mu = 2$$

9. (8)



$$r_{\text{A}} = k[\text{A}]; \quad k = \frac{\ln 2}{30}$$

$$P_{\text{A}} \rightarrow a = 5; P_{\text{D}} \rightarrow b = \frac{10}{5} = 2; c = 1$$

$$a + b + c = 8$$

10. (16)

$$k \times 8 = \ln \left[ \frac{1750-1000}{1750-1375} \right] \Rightarrow t_{1/2} = 8, t_{3/4} = 16$$

1. (B)

(b) Given  $-\frac{d[\text{MnO}_4^-]}{dt} = 4.56 \times 10^{-3} \text{ Ms}^{-1}$

From the reaction given,

$$-\frac{1}{2} \frac{d[\text{MnO}_4^-]}{dt} = \frac{4.56 \times 10^{-3}}{2} \text{ Ms}^{-1}$$

$$-\frac{1}{2} \frac{d[\text{MnO}_4^-]}{dt} = \frac{1}{5} \frac{d\text{I}_2}{dt}$$

$$\therefore -\frac{5}{2} \frac{d[\text{MnO}_4^-]}{dt} = \frac{d\text{I}_2}{dt}$$

On substituting the given value

$$\therefore \frac{d\text{I}_2}{dt} = \frac{4.56 \times 10^{-3} \times 5}{2} = 1.14 \times 10^{-2} \text{ M/s}$$

2. (D)

(d) For a zero order reaction,

$$[\text{A}_t] = [\text{A}_0] - k.t$$

$$\Rightarrow 0.5 = [\text{A}_0] - 2 \times 10^{-2} \times 25 \Rightarrow [\text{A}_0] = 1 \text{ M}$$

3. (B)

(b)  $X \rightarrow Y; \Delta H = -135 \text{ kJ/mol}$ ,

$$E_a = 150 \text{ kJ/mol}$$

For an exothermic reaction,

$$E_{a(\text{F.R.})} = \Delta H + E'_{a(\text{B.R.})}$$

$$\Rightarrow 150 = -135 + E'_{a(\text{B.R.})} \Rightarrow E'_{a(\text{B.R.})} = 285 \text{ kJ/mol}$$

4. (D)

(d) From rate law

$$-\frac{1}{2} \frac{d[\text{SO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$\therefore -\frac{d[\text{SO}_2]}{dt} = -2 \times \frac{d[\text{O}_2]}{dt} = -2 \times 2.5 \times 10^{-4}$$

$$= -5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

5. (C)

(c) Given  $t_{1/2} = 15$  minutes

Total time ( $T$ ) = 1 hr = 60 min

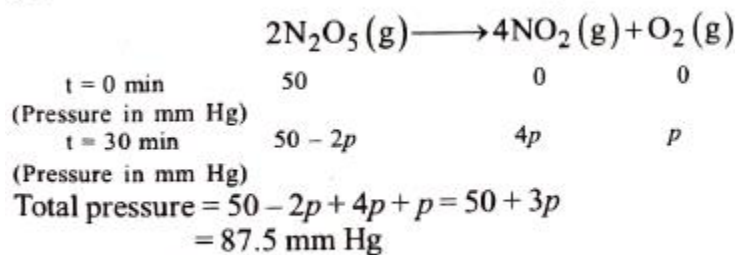
$$\text{From } T = n \times t_{1/2} \quad n = \frac{60}{15} = 4$$

$$\text{Now from the formula, } \frac{N}{N_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

6. (C)  
Reactions of higher order ( $>3$ ) are very rare due to very less chances of many molecules to undergo effective collisions.

7. (A)

(a) Rate law for first order reaction =  $k[\text{N}_2\text{O}_5]$



$$\therefore p = 12.5 \text{ mm Hg}$$

$$\therefore p_0 = 50$$

$$p(t = 30 \text{ min}) = 50 - 2 \times 12.5 = 25 \text{ for } \text{N}_2\text{O}_5 \text{ reactant}$$

$$\therefore k = \frac{2.303}{30 \text{ min}} \times \log\left(\frac{50}{25}\right) = \frac{2.303}{60 \text{ min}} \times \log\left(\frac{50}{x}\right)$$

$$\text{On solving } x = 12.5 \text{ mm Hg} = 50 - 2p_{60}$$

$$\therefore p_{60} = 18.75 \text{ mm Hg}$$

$$\therefore \text{Total pressure} = 50 + 3p = 106.25 \text{ mm Hg}$$

8. (C)

(c) Rate =  $k[\text{A}][\text{B}] = \text{R}$

$\text{R}' = k[\text{A}][2\text{B}]$

$$\frac{\text{R}}{\text{R}'} = \frac{k[\text{A}][\text{B}]}{k[\text{A}][2\text{B}]} = \frac{k[\text{A}][\text{B}]}{2k[\text{A}][\text{B}]}$$

$$\Rightarrow 2\text{R} = \text{R}', \text{ i.e., rate becomes double.}$$

9. (A)

(a)  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) \Delta\text{H} = -40 \text{ kJ}$

If activation energy of the reaction =  $x$

$$\text{since, } \frac{E_f}{E_b} = \frac{2}{3}, \text{ therefore, } E_f = \frac{2x}{5} \text{ and } E_b = \frac{3x}{5}$$

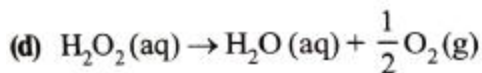
$$E_b - E_f = -\Delta\text{H} = +40 \Rightarrow \frac{3x}{5} - \frac{2x}{5} = 40 \Rightarrow x = 200$$

Therefore,

$$E_b = \frac{3x}{5} = \frac{3 \times 200}{5} = 120 \text{ kJ mol}^{-1}$$

$$E_f = \frac{2x}{5} = \frac{2 \times 200}{5} = 80 \text{ kJ mol}^{-1}$$

10. (D)



For a first order reaction,

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

Given  $a = 0.5$ ,  $(a-x) = 0.125$ ,  $t = 50$  min

$$\therefore k = \frac{2.303}{50} \log \frac{0.5}{0.125} \\ = 2.78 \times 10^{-2} \text{ min}^{-1}$$

$$r = k[\text{H}_2\text{O}_2] = 2.78 \times 10^{-2} \times 0.05 = 1.386 \times 10^{-3} \text{ mol min}^{-1}$$

Now

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{d[\text{H}_2\text{O}]}{dt} = \frac{2d[\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2]$$

$$\therefore \frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \times \frac{d[\text{H}_2\text{O}_2]}{dt}$$

$$= \frac{1.386 \times 10^{-3}}{2} = 6.93 \times 10^{-4} \text{ mol min}^{-1}$$

11. (D)  
Rate constant is independent of concentration.

12. (A)

$$(a) \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln 4 = \frac{E_a}{8.314} \left( \frac{310 - 300}{310 \times 300} \right)$$

$$2 \ln 2 = \frac{E_a}{8.314} \left( \frac{310 - 300}{310 \times 300} \right)$$

$$E_a = \frac{0.693 \times 2 \times 8.314 \times 300 \times 310}{10} = 107.2 \text{ kJ/mol}$$

13. (B)

$$(b) \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

For reaction A -

$$\text{Given, } \frac{k_2}{k_1} = 2, T_1 = 300 \text{ K}, T_2 = 310 \text{ K}$$

$$\log 2 = \frac{E_a^A}{2.303R} \left[ \frac{1}{300} - \frac{1}{310} \right] \quad \dots(i)$$

For reaction B -

$$\text{Given, } \frac{k_2}{k_1} = 2, E_a^B = 2E_a^A, T_1 = 300 \text{ K}, T_2 = ?$$

$$\log 2 = \frac{E_a^B}{2.303R} \left[ \frac{1}{300} - \frac{1}{T_2} \right] \quad \dots(ii)$$

From equation (i) and (ii),

$$\frac{2E_a^A}{2.303R} \left[ \frac{1}{300} - \frac{1}{T_2} \right] = \frac{E_a^A}{2.303R} \left[ \frac{1}{300} - \frac{1}{310} \right]$$

$$\Rightarrow 2 \left[ \frac{1}{300} - \frac{1}{T_2} \right] = \frac{310 - 300}{300 \times 310} \Rightarrow T_2 = 304.92 \text{ K}$$

$$T_1 = 300 \text{ K}, T_2 = 304.92 \text{ K}$$

$$\Delta T = T_2 - T_1 = 4.92 \text{ K.}$$

14. (D)

$$(d) k_1 = A \cdot e^{-E_{a1}/RT} \quad \dots(i)$$

$$k_2 = A \cdot e^{-E_{a2}/RT} \quad \dots(ii)$$

On dividing equation (ii) by (i)

$$\Rightarrow \frac{k_2}{k_1} = e^{\frac{(E_{a1} - E_{a2})}{RT}}$$

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{E_{a1} - E_{a2}}{RT} = \frac{10,000}{8.314 \times 300} = 4$$

15. (C)

(c) The half life  $t_{1/2} = 10$  days

The decay constant,

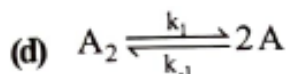
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \text{ days}} = 0.0693 \text{ days}^{-1}$$

The time required for one fourth conversion

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

$$= \frac{2.303}{0.0693 \text{ day}^{-1}} \log_{10} \frac{1}{1 - (1/4)} = 4.1 \text{ days}$$

16. (D)



$$-\frac{1}{2} \frac{d[A]}{dt} = k_{-1}[A]^2 - k_1[A_2] \Rightarrow \frac{d[A]}{dt} = 2k_1[A_2] - 2k_{-1}[A]^2$$

17. (C)

(c) For the reaction  $2X \rightarrow B$ , follow zeroth order

Rate equation is

$$Kt = [A]_0 - [A]$$

For the half-life;  $t = t_{1/2}$  and  $[A] = 0.1$

$$K t_{1/2} = 0.2 - 0.1$$

$$K = \frac{0.2 - 0.1}{6} = \frac{0.1}{6} \text{ M hr}^{-1}$$

$\therefore$  Time required to reach from 0.5 M to 0.2 M = t

$$Kt = [A]_0 - [A]$$

$$\frac{0.1}{6} \times t = (0.5 - 0.2) \Rightarrow t = 18 \text{ hour}$$

18. (A)

(a) Rate constant of decomposition of  $X = 0.05 \mu\text{g/year}$ .

Unit of rate constant confirms that the decomposition of  $X$  is a zero order reaction.

For zero order kinetics,

$$[X] = [X]_0 - kt$$

$$kt = [X]_0 - [X]$$

$$t = \frac{[X]_0 - [X]}{k} \quad t = \frac{5 - 2.5}{0.05} = \frac{2.5}{0.05} = 50 \text{ years}$$

19. (C)

(c)  $xA \rightarrow yB$

$$\therefore \frac{-dA}{xdt} = \frac{1}{y} \frac{dB}{dt} \Rightarrow \frac{-dA}{dt} = \frac{dB}{dt} \times \frac{x}{y}$$

$$\log \left[ \frac{-dA}{dt} \right] = \log \left[ \frac{dB}{dt} \right] + \log \left( \frac{x}{y} \right)$$

Comparing this equation with the equation given in question. We get,

$$\log \frac{x}{y} = 0.3010 \quad \text{or} \quad \log \frac{x}{y} = \log 2$$

$$\therefore \frac{x}{y} = 2 \quad \therefore \text{The reaction is of type } 2A \rightarrow B.$$

Hence, option (c) is correct.



20. (B)  
**(b)** From Arrhenius equation,

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

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

slope =  $-y$  (given)

$$-y = -E_a \Rightarrow E_a = y$$

21. (A)

**(a)** So,  $\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\log \frac{1}{2.5 \times 10^{-4}} = \frac{E_a}{8.314 \times 2.303} \left( \frac{1}{600} - \frac{1}{800} \right)$$

$$\Rightarrow 3.6 = \frac{E_a}{8.314 \times 2.303} \times \frac{200}{600 \times 800} \Rightarrow E_a = 165.4 \text{ kJ/mol}$$

22. (D)

**(d)** Arrhenius equation :

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

$$\ln k = \ln A - \left( \frac{E_a}{R} \right) \frac{1}{T} \Rightarrow \ln k = \ln A - \left( \frac{E_a}{R \times 10^3} \right) \times \frac{10^3}{T}$$

$$\text{Slope of graph} = \frac{-E_a}{R \times 10^3} = \frac{-10}{5}$$

$$E_a = 2R \times 10^3 \text{ J} = 2R \text{ kJ}$$

23. (A)

**(a)** The rate constant of a reaction is given by,

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

The rate constant in presence of catalyst is given by,

$$k' = Ae^{-E'_a/RT}$$

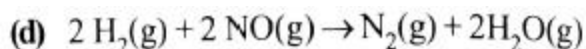
$$\frac{k'}{k} = e^{-(E'_a - E_a)/RT}$$

$$10^6 = e^{-(E'_a - E_a)/RT}$$

$$\ln 10^6 = -\frac{(E'_a - E_a)}{RT}$$

$$E'_a - E_a = -6(2.303)RT$$

24. (D)



$$R_f = K_f [\text{NO}]^2 [\text{H}_2]$$

This means that, for forward reaction the order of reaction w.r.t.  $[\text{NO}]$  is 2 and that w.r.t.  $[\text{H}_2]$  is 1.

Assuming the equilibrium expression,

$$K_{\text{eq}} = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{NO}]^2} = \frac{K_f}{K_b}$$

$$\Rightarrow K_f [\text{NO}]^2 [\text{H}_2] = K_b \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{H}_2]}$$

$$\text{At equilibrium, } R_f = R_b \Rightarrow R_b = K_b \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{H}_2]}$$

**Note:** In this question, the order of reaction for backward reaction is not given.

25. (C)

(c) For a given reaction,

$$\text{rate} = -\frac{1}{2} \frac{dn_A}{dt} = -\frac{1}{3} \frac{dn_B}{dt} = -\frac{2}{3} \frac{dn_C}{dt}$$

$$\text{rate} = \frac{dn_A}{dt} = \frac{2}{3} \frac{dn_B}{dt} = \frac{4}{3} \frac{dn_C}{dt}$$

26. (B)

$$(b) \quad C_t = C_0 e^{-kt}; \quad k = \frac{\ln 2}{t_{1/2}}$$

$$(C_t)_A = (C_0)_A e^{-k_A t}; \quad k_A = \frac{\ln 2}{300}$$

$$(C_t)_B = (C_0)_B e^{-k_B t}; \quad k_B = \frac{\ln 2}{180}$$

$$\frac{(C_t)_B}{(C_t)_A} = \frac{(C_0)_B}{(C_0)_A} \times e^{(k_B - k_A)t} \Rightarrow 4 = e^{(k_B - k_A)t}$$

$$\Rightarrow 2 \ln 2 = \left[ \frac{\ln 2}{180} - \frac{\ln 2}{300} \right] t \Rightarrow 2 \ln 2 = \ln 2 \left[ \frac{1}{180} - \frac{1}{300} \right] t$$

$$\Rightarrow 2 = \left( \frac{120}{180 \times 300} \right) t \Rightarrow t = \frac{2 \times 180 \times 300}{120} = 900 \text{ sec}$$

27. (C)

(c) Rate =  $k[A]^n$   
 comparing units

$$\frac{(\text{mol/L})}{\text{sec}} = k \left( \frac{\text{mol}}{\text{L}} \right)^n \Rightarrow k = \text{mol}^{(1-n)} \text{L}^{(n-1)} \text{s}^{-1}$$

28. (C)

(c) Given  $t_{0.90} = X t_{1/2}$   
 First order rate constant,

$$K = \frac{\ln 2}{t_{1/2}} = \frac{1}{X t_{1/2}} \ln \frac{A_0}{A_0 - A_0 \times \frac{90}{100}}$$

$$\frac{\ln 2}{t_{1/2}} = \frac{\ln 10}{X t_{1/2}} \Rightarrow X = \frac{\ln 10}{\ln 2} = \frac{2.303}{2.303 \times 0.3010} = 3.32$$

29. (C)

(c) For 1<sup>st</sup> order reaction

$$k = \frac{2.303}{t} \log \frac{a_0}{0.2a_0}$$

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

$$k = \frac{0.693}{200} \Rightarrow \frac{0.693}{200} = \frac{2.303}{t} \log \frac{1}{0.2}$$

$$t = \frac{2.303}{0.693} \times 200 \log \frac{1}{0.2} = 466.675 \approx 467 \text{ sec}$$

30. (60)

$$t = \frac{2.303}{k} \log \left[ \frac{100}{100 - x\%} \right] \quad t_{75\%} = \frac{2.303}{k} \log \left[ \frac{100}{25} \right] = 90$$

$$t_{60\%} = \frac{2.303}{k} \log \left[ \frac{100}{40} \right]$$

$$\frac{t_{75\%}}{t_{60\%}} = \frac{2 \log 2}{\log 2.5} \Rightarrow \frac{90}{t_{60\%}} = \frac{2 \times 0.3}{0.4}$$

$$\Rightarrow t_{60\%} = \frac{90 \times 4}{6} = 60 \text{ min.}$$

31. (84297.48)

(84297.48)

$$\because k = Ae^{-E_a/RT}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \Rightarrow \ln 5 = \frac{E_a}{R} \left( \frac{1}{300} - \frac{1}{315} \right)$$
$$\Rightarrow E_a = \frac{1.6094 \times 8.314 \times 300 \times 315}{15} = 84297.48 \text{ J/mol.}$$

32. (-3.98)

(-3.98) For a first order reaction,  $kt = \ln \frac{[A]}{[A_0]}$

At 300 K,  $k_1 \times 60 = \ln \frac{[A]}{[A_0]}$  ... (1)

At 400 K,  $k_2 \times 40 = \ln \frac{[A]}{[A_0]}$  ... (2)

From equation (1) and (2),

$$\frac{k_2}{k_1} = \frac{60}{40}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \left( \frac{60}{40} \right) = \frac{E_a}{8.3} \times \frac{100}{400 \times 300}$$
$$\Rightarrow E_a = -0.4 \times 8.3 \times 1200 = -3984 \text{ J/mol.} = -3.984 \text{ kJ/mol.}$$

33. (2)

$$(2) \quad k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\frac{2.303}{t_{50\%}} \log \frac{100}{100-50} = \frac{2.303}{t_{75\%}} \log \frac{100}{100-75}$$

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

34. (7)

(7) For the first order reaction

$$Kt = \ln \frac{[R]_0}{[R]}$$

$$K \times 60 = \ln \frac{(2.4 \times 10^{-2})}{(1.6 \times 10^{-2})} = 2.303 \times (\log 3 - \log 2) \frac{1}{60}$$

$$= 2.303 \times (0.477 - 0.301) \frac{1}{60}$$

$$\Rightarrow K = 6.7 \times 10^{-3} \text{ min}^{-1} \approx 7 \times 10^{-3} \text{ min}^{-1}$$

35. (10)

(10) This question is incomplete, order is not given. If we consider, the given reaction to be first order, then

$$t_{1/2} = \frac{\ln 2}{k} \Rightarrow k = \frac{\ln 2}{t_{1/2}}$$

$$\therefore t = \frac{1}{k} \ln \frac{100}{100 - 99.9} \Rightarrow t = \frac{1}{\ln 2} \ln 10^3$$

$$\Rightarrow t = \frac{1 \times 3 \times \ln 10}{\ln 2} = \frac{3 \times 2.3}{0.69} = 10 \text{ min.}$$

36. (2)

A → Products

Rate constant of a first order is given as,

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{570} \log \frac{100}{32} = 2 \times 10^{-3} \text{ s}^{-1}$$

37. (45)

(45)  $\Delta H = \text{Energy of products} - \text{Energy of reactants}$

$$= Z - (Z + Y) = -45 \text{ kJ/mol}$$

$$|\Delta H| = 45 \text{ kJ/mol}$$

38. (47)

$$(47) \text{ Given, } \log K = 20.35 - \frac{2.47 \times 10^3}{T} \quad \dots(i)$$

$$\text{We know, } \log K = \log A - \frac{E_a}{2.303 RT} \quad \dots(ii)$$

Comparing equation (i) with equation (ii),

$$\frac{E_a}{2.303 RT} = \frac{2.47 \times 10^3}{T}$$

$$E_a = 2.47 \times 10^3 \times 2.303 \times 8.314$$

$$= 47293.44 \text{ J/mol} = 47 \text{ kJ/mol}$$

39. (52)

$$(52) \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$
$$\log 5 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{300} - \frac{1}{325} \right]$$
$$\Rightarrow E_a = 52271 \text{ J mol}^{-1} = 52.271 \text{ kJ mol}^{-1}$$

40. (1)

$$(1) t = \frac{1}{k} \ln \left( \frac{a}{a-x} \right)$$
$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{30} \Rightarrow 100 = \frac{30}{\ln 2} \ln \left( \frac{1}{w} \right)$$
$$\frac{1}{w} = 10 \Rightarrow w = 1 \times 10^{-1} \mu\text{g}$$

41. (165)

(165)

$t_{1/2} = 70$  min; for 1st order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{70 \times 60} \text{ s}^{-1} = \frac{6930}{7 \times 6} \times 10^{-6} \text{ s}^{-1} = 165 \times 10^{-6} \text{ s}^{-1}$$

42. (2)

(2)

- For zero order,  $t_{1/2}$  decrease with decrease in concentration of reactions.
- For first order,  $t_{1/2}$  is independent of concentration of reaction
- For second order,  $t_{1/2}$  increases with decrease in concentration of reactant.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left( \frac{[A_0]_2}{[A_0]_1} \right)^{1-n} \Rightarrow \frac{100}{50} = \left( \frac{0.5}{1.0} \right)^{1-n}$$
$$\Rightarrow 2 = \left( \frac{1}{2} \right)^{1-n} \Rightarrow 2 = 2^{n-1} \Rightarrow n-1=1 \Rightarrow n=2$$

43. (1)

Since the half life for the decomposition of gas is not dependent on initial concentration, the order of the reaction is one.

44. (16)

$$(16) t = \frac{1}{k} \ln \left( \frac{a_0}{a_0 - n} \right)$$

$$k = \frac{\ln(2)}{t_{1/2}} \quad t_{67\%} = \frac{1}{k} \ln \left( \frac{1}{1-0.67} \right) = \frac{t_{1/2}}{\ln 2} \times \ln \left( \frac{1}{1-\frac{2}{3}} \right)$$

$$t_{67\%} = \frac{t_{1/2}}{\log 2} \times \log 3 = \frac{t_{1/2} \times 0.4771}{0.301} \Rightarrow t_{67\%} = 1.585 \times t_{1/2}$$

$$x \times 10^{-1} = 1.585 \Rightarrow x = 15.85 \approx 16$$

45. (75)

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

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

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]_t}$$

$$t = \frac{t_{1/2}}{0.3} \log \frac{[A_0]}{[A]_t}$$

$$83 = \frac{200}{0.3} \log \frac{[A_0]}{[A]_t}$$

$$0.125 = \log \frac{[A_0]}{[A]_t}$$

$$\frac{[A_0]}{[A]_t} = 1.333 \cong \frac{4}{3}$$

$$\therefore \frac{[A]_t}{[A]_0} \times 100 = \frac{3}{4} \times 100 = 75\%$$

46. (200)

$$(200) k_A = \frac{\ln 2}{100}; k_B = \frac{\ln 2}{50}$$

$$A_t = A_0 \times e^{-k_A t}$$

$$A_t = A_0 \times e^{\left(\frac{-\ln 2}{100} \times t\right)}; B_t = B_0 \times e^{\left(\frac{-\ln 2}{50} \times t\right)}$$

$$\text{Given, } A_0 = B_0 \text{ and } A_t = 4B_t$$

$$e^{\frac{\ln 2}{100} \times t} = 4 \times e^{\frac{\ln 2}{50} \times t} \Rightarrow e^{\frac{\ln 2}{100} \times t} = 4$$

$$\Rightarrow \frac{\ln 2}{100} \times t = \ln 4 = 2 \ln 2 \Rightarrow t = 200 \text{ sec.}$$

47. (0)

$$(0) t_{1/2} \propto \frac{1}{[P_0]^{n-1}}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{(P_2)^{n-1}}{(P_1)^{n-1}} \Rightarrow \frac{340}{170} = \left(\frac{27.8}{55.5}\right)^{n-1}$$

$$\Rightarrow 2 = \frac{1}{(2)^{n-1}} \Rightarrow n = 0$$

48. (225)

$$(225) k = A e^{\frac{-E_a}{RT}}$$

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

$$\Rightarrow \log(2 \times 10^{-6}) = \log(4 \times 10^{13}) - \frac{8.3 \times 10^3}{8.3 \times T \times 2.3}$$

$$\Rightarrow \log(2) - 6 = 2 \times \log(2) + 13 - \frac{8.3 \times 10^3}{8.3 \times T \times 2.3}$$

$$\Rightarrow -19.3 = -\frac{10^3}{T \times 2.3} \Rightarrow T = 225 \times 10^{-1} \text{ K}$$

49. (216)

$$(216) K = A e^{-E_a/RT} = (6.5 \times 10^{12} \text{ s}^{-1}) e^{-26000 \text{ K}/T}$$

$$\frac{E_a}{8.314} = 26000 \Rightarrow E_a = 216.164 \text{ kJ/mol.}$$

50. (59)



$$(59) \log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$T_1 = 300\text{K}, T_2 = 309\text{K}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{1}{300} - \frac{1}{309} \right)$$

$$0.3 = \frac{E_a}{2.303 \times 8.3} \left( \frac{9}{300 \times 309} \right)$$

$$E_a = \frac{0.3 \times 2.303 \times 8.3 \times 300 \times 309}{9} = 59065.04\text{J/mol}$$

$$E_a = 59.06 \text{ kJ/mol}$$

51.

(4)

(4) According to the Arrhenius equation

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

$$K_{\text{cat}} = Ae^{\frac{E_a^1}{RT}}, \quad K_{\text{uncat.}} = Ae^{\frac{E_a}{RT}}$$

$$\frac{K_{\text{cat}}}{K_{\text{uncat.}}} = e^{\frac{E_a - E_a^1}{RT}} = e^{\frac{10 \times 1000}{8.3 \times 300}} = e^{4.009} = e^x$$

$$[E_a - E_a^1 = 10 \text{ kJ}]$$

$$\therefore x = 4$$

## Exercise - 2A

1. order w.r.t A is 1 [from (i) & (ii)]

w.r.t B is 0

$$\text{rate} = k\{A\}$$

$$k = \frac{0.005}{0.01} = 0.5 \quad t_{1/2} = \frac{0.693}{k} = 1.386 \text{ min}$$

2. As it is 1<sup>st</sup> order  $r \times n$

$$t = \frac{2.303}{k} \log \frac{\{A_0\}}{\{A_t\}}, \quad \{A_0\} = 0.5 \text{ m} \quad \{A_t\} = 0.05 \text{ m}$$



3.  $t = 0$     80    0    0

at  $t = 20$      $80 - x$      $x$      $x$

$$80 + x = 120 \Rightarrow x = 40 \text{ min} \quad \text{So } t_{1/2} = 20 \text{ min}$$

$$4. \quad t_{1/2} \propto \frac{1}{a} \quad \text{so } n = 2 \quad \text{as } \left( t_{1/2} \propto \frac{1}{a^{n-1}} \right)$$

$$5. \quad K = A e^{-E_a/RT} \log_e \left( \frac{k_1}{k_2} \right) = -\frac{E_a}{k} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

$$E_a = R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \ln \left( \frac{k_2}{k_1} \right)$$

$$6. \quad E_{a_f} - E_{a_b} = \Delta H < 0 \quad \text{for } E_{a_b} > E_{a_f}$$

$$\text{So in 4<sup>th</sup> } r \times n \quad \Delta H = -40 \text{ kcal}$$

7. for  $A \rightarrow$  product

for  $2R \rightarrow$  Product

3 half life in 60 min

$$4 - \xrightarrow{1^{st} \text{ 20min}} 2 - \xrightarrow{2^{nd} \text{ 40min}} 1$$

$$4 - \xrightarrow{1^{st} \text{ 20min}} 2 - \xrightarrow{2^{nd} \text{ 20}} 1 - \xrightarrow{3^{rd} \text{ 20}} 0.5$$

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

$$t_{1/2} = \text{const}$$

only  $2t_{1/2}$  in 60 min

$$A \rightarrow B + C$$

8.  $t = 0 \quad 100 \quad 0 \quad 0$   
 $t = 10 \quad 100 - x \quad x \quad x$

$$100 + x = 120 \quad x = 20 \quad k = \frac{2.303}{10} \log \left( \frac{100}{100 - x} \right)$$

9. 1<sup>st</sup> order overall

$$t_{1/2} = \frac{0.693}{2.31 \times 10^{-3}} = 300 \text{ sec}$$

$$(B + A) \xrightarrow{t_{1/2}} \frac{(A + B)}{2} \xrightarrow{t_{1/2}} \frac{(A + B)}{4} \quad 2t_{1/2} = 600 \text{ sec}$$

10.  $\frac{k_1}{k_2} = \frac{\log(x_0/x_t)}{\log(y_0/y_t)} = \frac{\log(2)}{\log(100/4)} = 0.215 \quad \frac{k_2}{k_1} = 4.65$

11.  $k_1 = \frac{0.693}{(t_{1/2})_1}, k_2 = \frac{0.693}{(t_{1/2})_2} \quad Ea = R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \ln \left( \frac{k_2}{k_1} \right)$

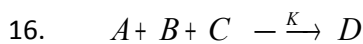
12.  $e^{-Ea/RT} = 3.8 \times 10^{-18} \quad (as \% = 3.8 \times 10^{-16})$

$$Ea = -RT \ln(3.8 \times 10^{-18})$$

13. As per theory

14. As derived in theory

15. as per theory



$$\mu \{B\}^1$$

$$\text{Rate} \mu \{A\}^0$$

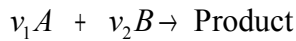
$$\mu \{C\}^1 \{B\}^1 \Rightarrow \text{rate} = k \{B\} \{C\} \quad \text{order} = 1 + 1 = 2$$

17.  $\frac{\{B\}}{\{B\} + \{C\}} \times 100 = \frac{k_1}{k_1 + k_2} \times 100 = 76.83\%$

18.  $\frac{k_1^1}{k_1} e^{-Ea_1 \left( \frac{1}{T_2} - \frac{1}{T_1} \right)} \Rightarrow \log_e \frac{k_1^1}{k_1} = Ea_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\text{As } E_{a_1} > E_{a_2}, \frac{k_1^1}{k_1} > \frac{k_2^1}{k_2}$$

19. rate =  $k\{A\}$



$$t = 0 \quad \{A\}_0 \quad \{B\}_0$$

$$\text{at } t \quad \{A\}_0 - v_1x$$

$$\frac{1}{v_1} + \left( V_1 \frac{dx}{dt} \right) = k_1\{A\} = k_1(\{A\}_0 - v_1x)$$

$$\Rightarrow \int_0^x \frac{dx}{\{A\}_0 - v_1x} = k_1 \int_0^t dt \quad k \Rightarrow v_1 \frac{1}{v_1} \ln \left( \frac{\{A\}_0}{\{A\}_0 - v_1x} \right) = k_1t$$

20.  $C_A$  is independent on R,  $k_2$  & S

21.  $\frac{k_{cat}}{k_{concat}} = e^{-\frac{(E_{a_{cat}} - E_{a_{concat}})}{RT}}$

22.  $t_{1/2} \propto C_0^{1-n}$  so  $n = 0.5$

23.  $t_{1/2} = 10 \text{ min}$  so  $C_t = 5 \text{ mol}$

$$\text{Rate} = kC_t = 5 \times 6.0693 \text{ mol min}^{-1}$$

24.  $-\frac{1}{2} \frac{d\{MnO_n^-\}}{dt} = \frac{1}{5} \frac{d\{I_2\}}{dt}$

25. As per theory, molecularity has no meaning for complex reaction

## Exercise - 2B

1. (A)  $S \Rightarrow$  first order (C) rate = constant

2. (A)  $\frac{6.55 - 0.31}{30} = 4.67 \times 10^{-3} \text{ Ms}^{-1}$  (C)  $k = \frac{\text{rate}}{\{\text{ester}\}}$

3. As per theory

4.  $\log k = \log A - \frac{Ea}{2.303RT} = \log k = 5 - \frac{2000K}{T}$

$$A = 10^5, Ea = 2000 R \times 2.303 = 9.152 \text{ kcal}$$

5. As per theory

6. As per theory

7. if  $Ea = 0$   $k = a$  or  $T \rightarrow \infty$   $e^{-Ea/Rt}$

$$8. \quad t_{1/2} = \frac{0.693}{k} \left( 1^{st} \text{ order} \right) = 0.693 \text{ toug}$$

$$9. \quad \text{As } t_{1/2} = \text{const. when } pH = \text{const i.e. } \{H^+\} = \text{const}$$

Rate  $\propto \{2n\}$ , rate  $\propto \{H^+\}^2$  as  $pH \rightarrow 3 - 2 \text{ rate} \rightarrow 100 \text{ time}$

$$\text{rate} = k \{zn\} \{H^+\}^2$$

$$10. \quad k = Ae^{-Ea/RT} \quad k \text{ only T dependent}$$

## Matix match

$$1. \quad (A) \quad t_{\frac{63}{64}} = t_{\left(1 - \frac{1}{2^6}\right)} \text{ means after } 6t_{\frac{1}{2}}$$

$$(B) \quad t_{\frac{15}{16}} = t_{\left(1 - \frac{1}{2^4}\right)} \text{ means after } 4t_{\frac{1}{2}} \text{ or } 2t_{\frac{3}{4}}$$

$$(C) \quad t_{\frac{31}{32}} = t_{\left(1 - \frac{1}{2^5}\right)} = 5t_{\frac{1}{2}}$$

$$(D) \quad t_{\frac{255}{256}} = t_{\left(1 - \frac{1}{2^8}\right)} = 2t_{\left(1 - \frac{1}{2^4}\right)} = 2t_{\frac{15}{16}}$$

$$2. \quad \frac{k_{308}}{k_{298}} = \text{temp coeff. (6y definition)}$$

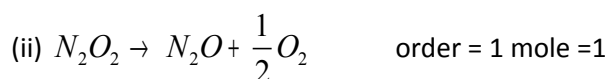
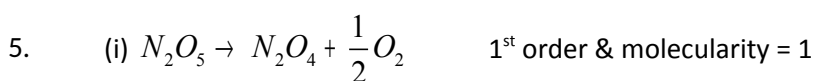
$$k = Ae^{-Ea/RT} \Rightarrow \log \frac{k_1}{k_2} = \frac{Ea}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

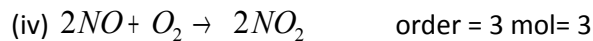
$$t_{99.9\%} = \frac{2.303}{K} \log \left( \frac{100}{100 - 99.9} \right) = \frac{6.93}{k} = 10t_{\frac{1}{2}}$$

3. As per theory

$$4. \quad t_{1/2} \propto \frac{1}{a^{n-1}}, n = \text{order t}$$

$$\text{Unit of } k = \frac{\text{rate}}{\{\text{conc}\}^n} = \text{mol}^{1-n} \text{lit}^{1-n} \text{ml}^{-1}$$





## Passage

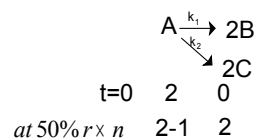
1, 2. Slower step is r.d.s

3.  $rate = k\{O\}\{O_3\}$  from 1<sup>st</sup> r × n  $k_{eq} = \frac{\{O_2\}\{O\}}{\{O_3\}}$

$$\{O\} = k_{eq} \frac{\{O_3\}}{\{O_2\}} \quad rate = k_{eq} \{O_3\}^2 \{O_2\}^{-1}$$

6.  $k = Ae^{-Ea/RT}$        $A = 10^{-4} e^{\frac{30,000}{8.314 \times 320}} = 79 = \text{maximum value of } K \text{ at } T \rightarrow \infty$

7 & 8    u



At 50% total moles = 1+2 = 3

$$\frac{k_1}{k_2} = \frac{\{B\}}{\{C\}} = \frac{1}{2} \quad \{C\} = 2\{B\} \quad \{C\} + \{B\} = 2$$

$$\{B\} = \frac{2}{3} = 0.666$$

## Integer Type

1.  $rate = k\{NOCl_2\}\{NO\}$

$$K_{eq} = \frac{\{NOCl_2\}}{\{NO\}\{Cl_2\}} \quad rate = k k_{eq} \{NO\}^2 \{Cl_2\}$$

Order = 2 + 1 = 3

2.  $P \rightarrow \text{Product } Q \rightarrow \text{Product} \quad t_{1/2} = 54 \text{ min} \quad t_{1/2} = 18 \text{ min}$

For 54 min  $P \rightarrow 1t_{1/2} \rightarrow \frac{P}{2} \quad Q \rightarrow 3t_{1/2} \rightarrow \frac{Q}{8}$

$$\frac{P}{Q} = 4$$

3.  $\text{Slope} = -\frac{Ea}{R} = \tan 45 \Rightarrow Ea = R = 2$

4.  $\log_{10} \left( \frac{dx}{dt} \right) = \log_{10} k + \log_{10} (a-x)^n \quad \log_{10} k = 0.6021 \Rightarrow k = 4$

5.  $Ea_f - Ea_b = \Delta H$

6.  $t_{1/2} \propto \frac{1}{a^4} = \frac{1}{a^{n-1}}$

$n=5$

7.  $\text{rate} \propto \{A\}^2 \Rightarrow \text{rate} = k\{A\}^2\{B\}$   
 $\propto \{B\}$

8.  $t_{1/2} \propto \frac{1}{a^3} \Rightarrow \frac{1}{a^{n-1}} \Rightarrow n = 4$

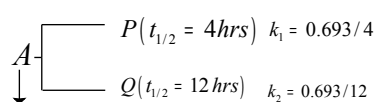
9.  $a_t = \frac{a_0}{2 \left( \frac{t}{t_{1/2}} \right)^2}$



$(t_{1/2})_B - (t_{1/2})_A = 6hrs$

11.  $\frac{k_{cat}}{k_{concat}} = 36 = e^{-(Ea_{cat} - Ea_{concat})/RT}$

12.



$t_{1/2} = \frac{0.693}{(k_1 + k_2)} = 3hrs$

## Exercise - 2 (C)

$$1. \quad -\frac{d\{N_2\}}{dt} = -\frac{1}{3} \frac{d\{H_2\}}{dt} = \frac{1}{2} \frac{d\{NH_3\}}{dt}$$

$$(a) \frac{\Delta\{N_2\}}{\Delta t} = 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1} \quad (b) \frac{\Delta\{H_2\}}{\Delta t} = 3 \times 10^{-4} \text{ M s}^{-1}$$

$$2. \quad \text{Rate} = -\frac{d\{N_2O_5\}}{dt} = \frac{1}{2} \frac{d\{NO_2\}}{dt} = 2 \frac{d\{O_2\}}{dt} = k\{N_2O_5\}$$

$$\Rightarrow k_1\{N_2O_5\} = \frac{1}{2} K_2\{N_2O_5\} = 2K_3\{N_2O_5\} \Rightarrow 2k_1 = k_2 = 4k_3$$

$$3. \quad (i) \text{ rate} = \frac{1}{4} \frac{\{\Delta NO\}}{\Delta t} = \frac{1}{4} \times \frac{1.08 \times 10^{-2}}{3} = 9 \times 10^{-4} \text{ mol lit}^{-1} \text{ sec}^{-1}$$

$$(ii) \text{ rate} = \frac{1}{4} \frac{\{\Delta NH_3\}}{\Delta t} = 9 \times 10^{-4} \rightarrow \frac{\Delta\{NH_2\}}{\Delta t} = 36 \times 10^{-4} \text{ mol lit}^{-1} \text{ s}^{-1}$$

$$(iii) \frac{\Delta\{H_2O\}}{\Delta t} = 54 \times 10^{-4} \text{ mol lit}^{-1} \text{ s}^{-1}$$

$$4. \quad -\frac{d\{H_2O_2\}}{dt} = \frac{d\{H_2O\}}{dt} = 2 \frac{d\{O_2\}}{dt} = 2 \times 3.6 \text{ M min}^{-1}$$

$$5. \quad \text{rate} = -\frac{1}{2} \frac{\Delta\{A\}}{\Delta t} = \frac{1}{2} \frac{0.4 - 0.5}{10} = 0.005 \text{ M min}^{-1}$$

$$6. \quad \text{rate} = k\{A\}^2$$

$$(a) A \rightarrow \frac{1}{3} A$$

$$\text{rate} \propto \{A\}^2 \quad \text{rate} \rightarrow \frac{1}{9} \text{ times}$$

$$(b) A \rightarrow \frac{2}{3} A \quad \text{rate} \rightarrow \frac{4}{9} \text{ times}$$

$$7. \quad \text{rate} \propto \{NO\}^2 \{O_2\} \propto \left(\frac{1}{V}\right)^2 \left(\frac{1}{V}\right) \propto \frac{1}{V^3} \quad \text{rate} \rightarrow (4)^3 \text{ if } v \rightarrow \frac{v}{4} \Rightarrow 64 \text{ times}$$

$$8. \quad (a) \text{ if } k_1 C \gg 1 \quad \frac{dC}{dt} = \frac{k_1}{k_2} \quad \text{order} = 0$$

$$(b) \text{ if } k_2 C \ll 1 \quad \frac{dc}{dt}; k_1 C \quad \text{order} = 1$$

$$9. \quad (i) \frac{dx}{dt} = k\{A\}\{B\}^2$$



(ii)  $A \rightarrow 2A$  &  $B \rightarrow 2B$       rate  $\Rightarrow$  8 times

10. rate =  $k \{A\}^2 \{B\}$   
           $\downarrow$       $\downarrow$             total = 2 + 1 = 3  
          2     1

11.  $\frac{dx}{dt} = k \Rightarrow \Delta x = k \Delta t$

(a) after 10 min i.e 600 sec  $\Delta x = k \times 600 = 7.2 M$

(b) after 20 min i.e 1200 sec  $\Delta x = k \times 120 = 15 M$  (which is not possible because all reactant have finished when  $\Delta x$ ;  $10 M$ )

12.  $\Delta x = k \Delta t = x = 2 \times 10^{-2} \times 25 = 0.5$

$a - x = 0.25 M \Rightarrow a = 0.75 M$

13. 1 hour  $\Rightarrow$  75%

for 90%  $\Rightarrow \frac{90}{75} \times 1 \text{ hour} = 1.2 \text{ hr}$

14. 1<sup>st</sup> order 75%  $\rightarrow$  72 min 50%  $\rightarrow$  36 min

(i) 36 min

(ii)  $A \xrightarrow{t_{1/2}} \frac{A}{2} \xrightarrow{t_{1/2}} \frac{A}{4} \xrightarrow{t_{1/2}} \frac{A}{8}$   $3t_{1/2} \rightarrow$  for 87.5 108 min

15. 1<sup>st</sup> order  $k = \frac{2.303}{t} \log \frac{\{A_0\}}{\{A_t\}}$

(a)  $k = \frac{2.30}{10} \log \left( \frac{100}{100 - 20} \right) = 2.23 \times 10^{-2} \text{ min}^{-1}$

(b)  $t = \frac{2.303}{2.23 \times 10^{-2}} \log \left( \frac{100}{100 - 75} \right) = 62.17 \text{ min}$

16.  $t_{99.9\%} = \frac{2.303}{K} \log \left( \frac{100}{100 - 99.9} \right) = \frac{6.9}{k} = 10 \times \frac{0.69}{k} = 10t_{1/2}$

17. 1<sup>st</sup> order  $\Rightarrow t_{1/2} = \text{constant}$

$$t_{1/2} = \frac{0.693}{1.5 \times 10^{-3}} = 462 \text{ sec}$$

$$5 \text{ g} \xrightarrow{t_{1/2}} 2.5 \text{ g} \xrightarrow{t_{1/2}} 1.25 \text{ g}$$

$$t = 2t_{1/2} = 924 \text{ sec}$$

18.

$$\frac{dN}{Ndt} \times 100 = 2\%$$

$$\frac{dN}{Ndt} = 0.02 / \text{min}$$

$$19. \quad kt = 2.303 \log \left( \frac{100}{100 - 90} \right)$$

$$\frac{0.693}{50} \times t = 2.303 \log 10$$

$$t = 166.16 \text{ min}$$

$$20. \quad kt = 2.303 \log \frac{\{A_0\}}{\{A_t\}}$$

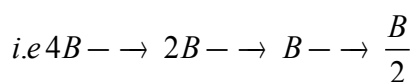
$$\frac{\{A_t\}}{\{A_0\}} = 0.0526$$

$$t_{1/2} = \frac{0.693}{k} = 9.62 \times 10^5 \text{ sec}$$

$$21. \quad \text{(i) } t = \frac{2.303}{k} \log \frac{\{A_0\}}{\{A_t\}} = 13.96 \text{ hr} \quad \left( k = \frac{0.693}{t_{1/2}} \right)$$

$$\text{(ii) } n_{N_2O} ; \frac{6.2}{12} = 0.1 \text{ mol} ; 2.2176 \text{ lit}$$

$$22. \quad A \xrightarrow{5\text{min}} \frac{A}{2} \xrightarrow{5\text{min}} \frac{A}{4} \xrightarrow{5\text{min}} \frac{A}{8} = 15 \text{ min}$$



$$B \xrightarrow{15\text{min}} \frac{B}{2} = 15 \text{ min}$$

$$23. \quad \text{(I) Initial rate} = 1 \times 1 \times 10^{-2} \text{ Ms}^{-1}$$

$$\text{(ii) } \{A\}_t = \{A_0\} e^{-kt} = 0.548 \text{ M}$$

$$\text{rate} = k\{A\} = 5.49 \times 10^{-3} \text{ Ms}^{-1}$$

$$24. \quad t_{1/2} = 69.3 \text{ min}, \quad k = \frac{0.693}{69.3} = 10^{-2} \text{ min}^{-1} \quad t = \frac{2.303}{10^{-2}} \log \left( \frac{100}{20} \right) = 160.9 \text{ min}$$

$$25. \quad \frac{t_{99\%}}{t_{90\%}} = \frac{\log(100/1)}{\log(100/10)} = 2$$

26.  $\{A_t\} = \{A_0\} e^{-kt} = 0.7633M$

rate =  $k\{A_t\} = 3.43 \times 10^{-3} Ms^{-1}$

27.  $rate = k\{NO\}^2\{Cl_2\}$

28.  $t = \frac{2.303}{3.3 \times 10^{-4}} \log\left(\frac{100}{60}\right)$  ; 26 min

29. (A)  $rate \propto \{NO\}^2$  (from (ii) & (iii))

$rate \propto \{H_2\}$  (from (i) & (ii))

$rate = k\{NO\}^2\{H_2\}$  order = 3

(B)  $rate = k\{NO\}^2\{H_2\}$

(C)  $k = 4.88 \times 10^6$ ,  $rate = 1.21 \times 10^{-2} Ms^{-1}$

30. (A)  $rate \propto \{Cl_2\}$  (from (i) & (ii))

$\propto \{NO\}^2$  (From (i) & (iii))

order = 1 + 2 = 3

(B)  $rate = k\{NO\}^2\{Cl_2\}$       (C)  $k = \frac{1 \times 10^{-3}}{(0.05)^2(0.05)} = 8 L^2 mol^{-2} s^{-1}$

(D)  $rate = 8 \times 0.2 \times (0.4)^2 = 0.256 Ms^{-1}$

31. It is zero order

as  $\frac{\Delta p}{\Delta t} = const.$

$k = \frac{\Delta p}{\Delta t} = \frac{(4 - 3.5) \times 10^3}{100} pa/s$

32.  $t_{1/2} \propto a^{1-n}$  if  $a \rightarrow \frac{a}{2}$ ,  $t_{1/2} \rightarrow \frac{1}{2} t_{1/2}$

$1 - n = 1$ ,  $n = 0$

33.  $0.12 - \frac{t_{1/2}}{10 \text{ hours}} \rightarrow 0.06 - \frac{t_{1/2}}{10 \text{ hours}} \rightarrow 0.03$

$t_{1/2} = constant \Rightarrow 1^{st} order$

$$k = \frac{0.12 - 0.06}{10} = 0.0693 \text{ m}^{-1}$$

34. Reaction 1

$$t_{1/2} = \text{const. } 1^{\text{st}} \text{ order}$$

Reaction 2

$$t_{1/2} \propto \frac{1}{a}, \quad n = 2$$

Reaction 3

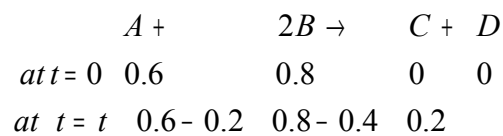
$$t_{1/2} \propto a, \quad n=0$$

35.  $\text{rate} \propto \{A\}$

$$\text{rate} = \{A\}$$

$$k = \frac{0.03}{0.1} = 0.3 \text{ s}^{-1}$$

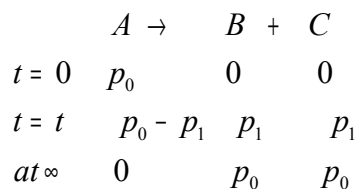
36.



$$\text{Rate} = k\{A\}\{B\}^2$$

$$\frac{(\text{rate})_t}{(\text{rate})_0} = \frac{(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$$

37.

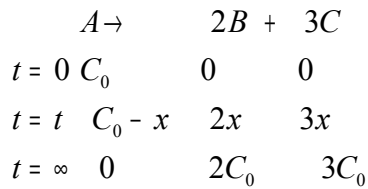


$$p_3 = p_{\infty} \quad p_{\infty} = 2p_0 \Rightarrow p_0 = \frac{p_{\infty}}{2} = \frac{p_3}{2}$$

$$p_2 = p_1 + p_1 \Rightarrow 2p_1$$

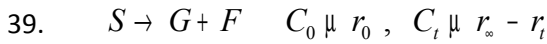
$$k = \frac{2.303}{t} \log \left( \frac{p_0}{p_0 - p_1} \right) = \frac{2.303}{t} \log \left( \frac{p_{\infty}}{p_{\infty} - p_2} \right) = \frac{1}{t} \ln \left( \frac{p_3}{p_3 - p_2} \right)$$

38.

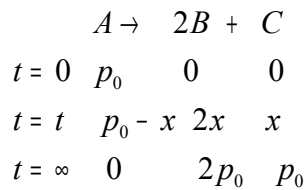


At time t  $V_2 = C_0 + 4x$   $x = \frac{V_2 - C_0}{4}$  at  $\infty$   $V_3 = 5C_0$

$$K = \frac{2.303}{t} \log \left( \frac{C_0}{C_0 - x} \right) = \frac{2.303}{t} \log \left[ \frac{V_3/5}{(V_3 - V_2)/4} \right]$$



40.

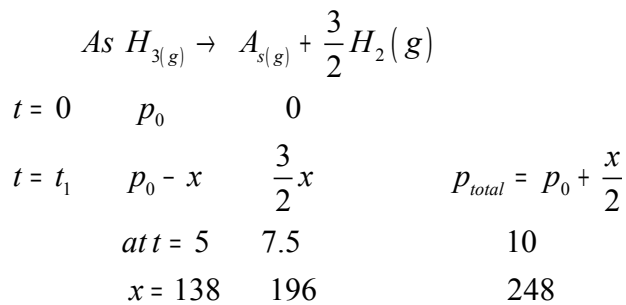


At 10 min  $176 = p_0 + 2x$   $270 = 3p_0 \Rightarrow p_0 = 90$   $x = 43$

(a) 90 mm of Hg (b)  $p_0 - x = 47$

(c)  $k = \frac{2.303}{t} \log \frac{\{A_0\}}{\{A_t\}}$  (d)  $\frac{0.693}{k}$

41.

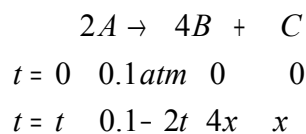


$$k = \frac{2.303}{t} \log \frac{\{A_0\}}{\{A_t\}} = \frac{2.303}{t} \log \left( \frac{p_0}{p_0 - x} \right)$$

if will be same for all value of x

42. As above

43.

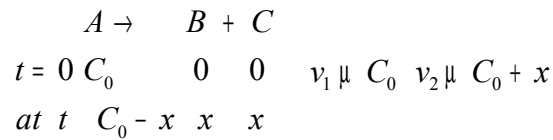


$$P_{\text{total}} = 0.1 + 3x = 0.145 \quad x = 0.015$$

$$t = \frac{2.303}{k} \log\left(\frac{0.1}{0.1 - 2x}\right) = 47.68s$$

$$p_t = p_0 e^{-kt} = 0.1 - 2x \quad P_{\text{total}} = 0.1 + 3x = 0.179 \text{ atm}$$

44.



$$k = \frac{2.303}{t} \log\left(\frac{v_1}{2v_1 - v_2}\right)$$

46.

$$\frac{\{B\}}{\{C\}} = \frac{k_1}{k_2} = \frac{1.26 \times 10^{-4}}{3.6 \times 10^{-5}} = 3.5$$

$$\frac{\{B\}}{\{B\} + \{C\}} = 0.7778 \Rightarrow 77.78\%$$

$$47. \quad t_{\text{max}} = \frac{1}{K_1 - k_2} \ln\left(\frac{k_1}{k_2}\right) = 4 \text{ min}$$

$$48. \quad (\text{a}) \text{ rate} = (k_1 + k_2 + k_3, \dots) \{A\}_t$$

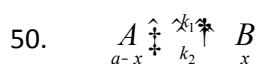
$$k = k_1 + k_2 + \dots k_n$$

(b) yes,

$$\text{As } \frac{d\{B\}}{dt} = k_2 \{A\}$$

$$\frac{d\{C\}}{dt} = k_3 \{A\}$$

49. As per theory



$$\frac{dx}{dt} = k_1(a-x) - k_2x = k_1 \left\{ (a-x) - \frac{k_2}{k_1}x \right\}$$

$$\Rightarrow \frac{dx}{dt} = k_1 \left( a - \frac{5}{4}x \right) \Rightarrow \int_0^x \frac{dx}{\left( a - \frac{5}{4}x \right)} = \int_0^{30} k_1 dt$$

$$\Rightarrow \frac{4}{5} \ln \left( \frac{a}{a - \frac{5}{4}x} \right) = 0.3 \Rightarrow \frac{a - \frac{5}{4}x}{a} = 0.687 \Rightarrow x = 2.5 \times 10^{-3}$$

51.  $E_a = 104.5 \text{ kJ/mol}$

$$A = 5 \times 10^{13} \text{ s}^{-1}$$

$$t_{1/2} = 1 \text{ min} \Rightarrow k = \frac{0.693}{60} = 0.01155 \text{ sec}^{-1}$$

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

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

52.  $E_a = R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \ln \left( \frac{k_2}{k_1} \right) = 55.32 \text{ kJ/mol}$

53.  $\frac{k_{308}}{k_{298}} = 1.75$

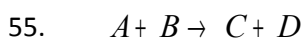
$$E_a = R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \log_e \left( \frac{k_2}{k_1} \right) = 10.22 \text{ kcal/mol}$$

54.  $\log_{10} k = 5.44 - \frac{212}{T} + 2.17 \log_{10} T$

Vont haff equation

$$\frac{d(\ln k)}{dt} = \frac{E_a}{RT^2}, \text{ comparing it with above}$$

$$E_a = 212 \times 2.303R + 2.17RT$$



$$E_f - E_b = \Delta H, \quad E_b = 85 - 20 = 65 \text{ kJ/mol}$$

56.  $k = \frac{0.693}{10 \times 60} = Ae^{-E_a/RT}$

57. as per theory

58.  $\Delta H = E_{a_f} - E_{a_b} = 32 - 58 < 0$  exothermic

59. (A)  $\Delta H = E_f - E_b > 0$  endo

(B)  $\Delta H$ ;  $20 \text{ kJ/mol}$  (c)  $E_{a_f} = 60 \text{ kJ/mol}$ ,  $E_{a_b} = 40 \text{ kJ/mol}$

(d) as  $E_a \rightarrow \text{decreases}$   $k \rightarrow \text{increase}$

60. 
$$E_a = R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \ln \left( \frac{K_2}{K_1} \right)$$

61. 
$$\frac{K_1}{K_2} = e^{\frac{-(E_{a_1} - E_{a_2})}{RT}}$$

62.  $k = A e^{-E_a/RT}$ ,  $e^{-E_a/RT} = 10^{-6}\% = 10^{-8}$

$$A = \frac{0.693}{100} \times 10^8 = 6.93 \times 10^5 \text{ sec}^{-1}$$

= maximum value of  $k$  at  $t \rightarrow \infty$

63. 
$$K_{eq} = \frac{\{NOBr_2\}}{\{NO\}\{Br_2\}}$$
 rate =  $k\{NO\}\{NOBr_2\} = k k_{eq}\{NO\}^2\{Br_2\}$

$$\text{Rate} = k^1\{NO\}^2\{Br_2\}$$

64. rate =  $k_2\{N_2O_5\}\{H_2\}$  (by r.d.s i.e. slow step)

$$= k_1 k_2\{NO\}^2\{H_2\}$$

65. 
$$\frac{k_1}{k^{-1}} = \frac{\{A\}^2}{\{A_2\}}$$

$$\text{rate} = k_2\{A\}\{C\}$$

$$= k_2 \left( \frac{k_1}{k-1} \right)^{1/2} \{A_2\}^{1/2} \{C\}$$

66. (A) step 2 as it is slower one

(B)  $(\text{rate})_2 = k\{O_3\}\{O\}$

(C) step1  $\rightarrow$  1, step = 2



Only One Option Correct

- (A)  
As per Arrhenius equation ( $k = Ae^{-E_a/RT}$ ), the rate constant increases exponentially with temperature.
- (D)  
**(d)** For P, if  $t_{50\%} = x$  then  $t_{75\%} = 2x$   
This is true only for first order reaction.  
So, order with respect to P is 1.  
Further, the graph shows that concentration of Q decreases with time. So, rate with respect to Q, remains constant.  
Hence, it is zero order wrt Q.  
So, overall order is  $1 + 0 = 1$
- (B)  
**(b)**  $M \rightarrow N$   
 $r = k[M]^x$   
when concentration =  $2M$ ; rate =  $8r$ , thus  
 $8r = k[2M]^x$   
 $8 = (2)^x$   
 $x = 3$

One or More than One Option Correct

- (B, C, D)  
(A) High activation energy usually implies a **slow reaction**.  
(B) Rate constant of a reaction increases with increase in temperature due to increase in number of collisions whose energy exceeds the activation energy.  
(C)  $k = P \times Z \times e^{-E_a/RT}$   
(D) So, pre-exponential factor  $(A) = P \times Z$  and it is independent of activation energy or energy of molecules.
- (A, B)  
According to Arrhenius equations  
 $k = Ae^{-E_a/RT}$   
Where, A = Frequency factor taking into account orientation factor,  
 $P = \frac{A}{Z}$  or  $A = PZ$   
 $k = PZe^{-E_a/RT}$   
Where, P = steric factor, Z = collision frequency  
The value of steric factor lies between 0 and 1 predicted by Arrhenius equation.  
Thus, the experimentally determined value of frequency factor higher than that predicted by Arrhenius equation. Thus, (B) is correct.
- (A, C)  
On increasing temperature, concentration of product decreases.

Hence, reaction is exothermic  $\Rightarrow \Delta H^\circ < 0$

$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > 1 \Rightarrow \ln K_{T_1} > \ln K_{T_2} \text{ so, } K_{T_1} > K_{T_2}$$

$$\text{Also, } \frac{\ln K_{T_1}}{\ln K_{T_2}} > \frac{T_2}{T_1}$$

$$\text{or } T_1 \ln K_{T_1} > T_2 \ln K_{T_2} \Rightarrow -RT_1 \ln K_{T_1} > -RT_2 \ln K_{T_2}$$

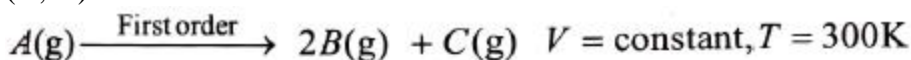
$$\text{or } \Delta G_{T_1}^\circ < \Delta G_{T_2}^\circ \quad (\because \Delta G = -RT \ln K)$$

$$\text{or } \Delta H^\circ - T_1 \Delta S^\circ < \Delta H^\circ - T_2 \Delta S^\circ$$

(Also  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ : Gibbs Helmholtz equation)

As  $T_1 < T_2$ , this is possible only when  $\Delta S^\circ < 0$

4. (A, D)



$$t = 0 \quad P_0$$

$$t = t_{1/3} \quad \left( P_0 - \frac{2P_0}{3} \right) \quad \frac{4P_0}{3} \quad \frac{2P_0}{3}$$

$$t = t \quad P_0 - x \quad 2x \quad x$$

So,  $P_t = P_0 - x + 2x + x = P_0 + 2x$   
 or  $2x = P_t - P_0$

$$\text{or } t = \frac{1}{k} \ln \frac{P_0}{P_0 - \frac{(P_t - P_0)}{2}} = \frac{1}{k} \ln \frac{2P_0}{2P_0 - P_t + P_0}$$

$$\text{or } kt = \ln \frac{2P_0}{3P_0 - P_t}, \quad kt = \ln 2P_0 - \ln(3P_0 - P_t)$$

$$\text{or } \ln(3P_0 - P_t) = -kt + \ln 2P_0$$

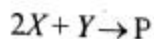
Graph between  $\ln(3P_0 - P_t)$  vs 't' is a straight line with negative slope.

Since, rate constant is a constant quantity and independent of initial concentration.

So, graph (a) and (d) are correct.

5. (B, C, D)

$$(b,c,d) \text{ Rate} = \frac{dP}{dt} = k[X]^1$$



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

$$t = 50 \text{ s} \quad 1 \text{ mol} \quad 0.5 \text{ mol} \quad 0.5 \text{ mol}$$

$$-\frac{1}{2} \frac{d[X]}{dt} = \frac{d[P]}{dt} = k[X]^1$$

$$-\frac{d[X]}{dt} = 2k[X]^1$$

$$2k = \frac{\ln 2}{50} \quad \Rightarrow \quad k = \frac{\ln 2}{100} = 6.93 \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{2k} = \frac{\ln 2 \times 50}{\ln 2} = 50 \text{ sec}$$

$$\begin{aligned} \text{At } 50 \text{ sec} \quad \frac{-d[X]}{dt} &= 2k \times (1)^1 = \frac{\ln 2}{50} \\ &= 13.86 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\text{At } 100 \text{ sec} \quad -\frac{1}{2} \frac{d[X]}{dt} = \frac{-d[Y]}{dt}$$

$$\Rightarrow -\frac{d[Y]}{dt} = \frac{\ln 2}{100} \times \frac{1}{2} \left\{ \frac{-d[Y]}{dt} = k[X]^1 \right\}$$

$$\frac{d[Y]}{dt} = 3.46 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

### Matrix-Match Type

1. (A)

$$(a) \text{ Rate} = \frac{k[X]}{X_s + [X]} = \frac{k}{\frac{X_s}{[X]} + 1} = k \frac{1}{\frac{X_s}{[X]} + 1}$$

(I) When  $[X]_0 \longrightarrow \infty$ ;  $\text{Rate} = k \Rightarrow \text{Rate}$  is independent of substrate's concentration.

$\therefore$  Order of reaction = 0

(I)  $\rightarrow$  (P), (S)

(II) When  $[X]_0 \ll X_s \therefore \text{Rate} = k \frac{[X]}{X_s}$

$\Rightarrow$  This implies Order of the reaction = 1.

(II)  $\rightarrow$  (Q), (T)

(III)  $[X]_0 \gg X_s$ ;  $[X] + X_s \approx [X]$

$$\text{Rate} = \frac{k[X]}{[X]} = k \Rightarrow \text{This implies Order of the reaction} = 0.$$

(III)  $\rightarrow$  (P), (S)

(IV)  $\text{Rate} = \frac{k[X]^2}{X_s + [X]}$

$[X] \gg X_s$ ;  $\text{Rate} = k[X] \Rightarrow \text{This implies Order of the reaction} = 1.$

(IV)  $\rightarrow$  (Q), (T)

### Integer Answer / Numerical Value Answer

1. (100)

(100) According to Arrhenius equation  $k = Ae^{-E_a/RT}$

Let  $E_a$  of the reaction in absence of catalyst =  $x \text{ kJ mol}^{-1}$

Therefore  $E_a$  of the reaction in presence of catalyst =  $x - 20 \text{ kJ mol}^{-1}$

The Arrhenius equations in the two conditions can thus be written as

$$k = Ae^{-\frac{x}{R \times 500}} \quad \dots(i)$$

$$k = Ae^{-\frac{x-20}{R \times 400}} \quad \dots(ii)$$

Dividing equation (i) by (ii), we get

$$e^{-\frac{x}{500R}} = e^{-\frac{x-20}{400R}} \Rightarrow \frac{x}{500} = \frac{x-20}{400} \text{ or } x = 100 \text{ kJ mol}^{-1}$$

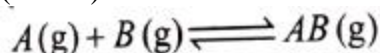
2. (9)

$$(9) \quad t_{1/8} = \frac{2.303 \log 8}{k} = \frac{2.303 \times 3 \log 2}{k}$$

$$t_{1/10} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$$

$$\left[ \frac{t_{1/8}}{t_{1/10}} \right] \times 10 = \frac{\left( \frac{2.303 \times 3 \log 2}{k} \right)}{\left( \frac{2.303}{k} \right)} \times 10 = 9$$

3. (-8500)



$$E_{ab} = E_{af} + 2RT \quad \text{and} \quad A_f = 4A_b$$

Now,

$$\text{Rate constant of forward reaction } k_f = A_f e^{-E_{af}/RT}$$

$$\text{Rate constant of reverse reaction } k_b = A_b e^{-E_{ab}/RT}$$

Equilibrium constant

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f}{A_b} e^{-(E_{af} - E_{ab})/RT}$$

$$K_{eq} = 4e^{2RT/RT} = 4e^2$$

$$\begin{aligned} \text{Now, } \Delta G^\circ &= -RT \ln K_{eq} = -2500 \ln (4e^2) \\ &= -2500 (\ln 4 + \ln e^2) = -2500 (1.4 + 2) \\ &= -2500 \times 3.4 = -8500 \text{ J/mol.} \end{aligned}$$

4. (6.75)

$$\text{Rate of the reaction} = K[A]^x[B]^y[C]^z$$

Comparing experiment 1 with 2 we get that,  $y=0$

Comparing experiment 1 with 3 we get that,  $z=1$

Comparing experiment 1 with 4 we get that,  $x=1$

putting values of  $x, y, z$  in rate equation for experiment 1.

$$6 \times 10^{-5} = K \times (0.2)^1 \times (0.1)^1 \times (0.1)^0$$

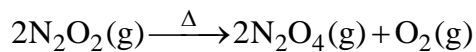
$$K = 3 \times 10^{-3}$$

Now, for the given concentration of  $A, B$  and  $C$ , rate of reaction will be,

$$\text{Rate} = 3 \times 10^{-3} \times 0.15 \times 1 \times 0.15 = 6.75 \times 10^{-5}$$

Therefore, value of  $Y = 6.75$ .

5. (2.30)

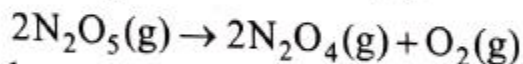


Given rate constant of the reaction =  $5 \times 10^{-4} \text{sec}^{-1}$

Thus, it is a first order reaction.

$$\frac{1}{2} \frac{dP_{\text{N}_2\text{O}_5}}{dt} = K_{\text{overall}} P_{\text{N}_2\text{O}_5}$$

$$\Rightarrow \frac{dP_{\text{N}_2\text{O}_5}}{dt} = 2K_{\text{overall}} P_{\text{N}_2\text{O}_5}$$



$$1-x \qquad \qquad x \qquad \qquad x/2$$

$$t = Y \times 10^3 \text{ sec.}$$

$$1 + \frac{x}{2} = 1.45$$

$$x = 0.90 \text{ atm}$$

For a first order reaction,

$$t = \frac{2.303}{K} \log \frac{[P]_0}{[P]}$$

$$t = \frac{2.303}{2K} \log \frac{[P]_0}{[P]}$$

$$Y \times 10^3 = \frac{2.303}{2 \times 5 \times 10^{-4}} \log \frac{1}{0.1}$$

$$Y = \frac{23.03}{10} = 2.30$$