Exercise - 1 (A)

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

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

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

4. relative strength µ rate constant

5. For $xA + yB \rightarrow zC \quad -\frac{1}{x}\frac{d\{A\}}{dt} = -\frac{1}{y}\frac{d\{B\}}{dt} = \frac{1}{2}\frac{d\{C\}}{dt}$

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

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

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

9. conc. µ $\frac{1}{V}$ so rate µ $\frac{1}{V^3}$

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

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

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

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

14. as per theory

15. rate $= k\{A\}\{B\}$ $i.e\,rate$ µ $n_A\ n_B$

16. rate constant is independent of number of moles

17. rate is independent of concentration of reactants

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

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

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

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

Pseudo-unimolecular

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

23. as question number 22

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

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

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

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

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

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

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

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

31. As reaction is zeroth order, rate = constant

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

32. As per theory

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

41 $a - x = ae^{-kt}$

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

42. log T_{50} is independent on log a hence 1st order reaction.

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

44. Unit of rate constant for 1st order is $\sec^{-1}$

45. $x = kt$

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

a = 1.0 M

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

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

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

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

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

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

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

52. As per theory

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

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

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

54. As per derivation

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

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

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

58. rate is independent on conc.

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

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

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

61.

$$\begin{array}{llll} & A \rightarrow & 2B \; + & C \\ t=0 & p_0 & 0 & 0 \\ t=10 & p_0 - x & 2x & x \\ t=\infty & 0 & 2p_0 & p_0 \end{array}$$

at $3P_0 = 270 \Rightarrow P_0 = 90\,mm\,of\;Hg$ t = 10 $P_0 + 2x = 176 \Rightarrow \quad x = 43$

So $p_0 - x = 90 - 43 = 47\,mm$

62. As per theory

63. As per theory

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

65. As per theory

66.

$$\begin{array}{llll} & A_{(g)} \rightarrow & B_{(g)} \; + & C_{(g)} \\ t=0 & P_0 & 0 & 0 \\ t=0\min & p_0 - x & x & x \end{array}$$

$p_0\,tx = 120 \quad x = 20\,mm$

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

67.

$$\begin{array}{llllll} & A_{(g)} & + \quad 2B_{(b)} & \Rightarrow \quad C_{(g)} & + \; D_{(g)} \\ t=0 & 0.6 & 0.8 & 0 & 0 \\ at\,t & 0.6-0.2 & 0.8-0.4, & 0.2, & 0.2 \end{array}$$

$$\frac{(rate)\,t}{(rate)\,t_0} = \frac{(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{64}{6\times 64} = \frac{1}{6}$$

68.

$$\begin{array}{llll} & A \rightarrow & B & + \quad C \\ t = 0 & 100 & 0 & 0 \\ t = 10 & 100 - x & x & x \end{array}$$

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

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

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

74. As per theory

75. 1st 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. $\frac{Ea}{2.303RT} = \frac{2000}{T} \Rightarrow E_a \approx 9.16\,kcal$

85. For exothermic $r \times n$

$Ea_f - Ea_b = -200\,kJ \quad Ea_b$ = 280 kJ

86. $Ea_f - Ea_b = -20\,kJ$

87. $Ea_f - Ea_b = -30$

88. $Ea_f - Ea_b = -10$

89. $x - Ea_b = y \Rightarrow Ea_b = x - y$

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

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

Slope = $-\frac{Ea}{2.303R} = \frac{1}{2.303}$ ⇒ Ea = 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. $\frac{k_1}{k_2} = e^{-\frac{(Ea_1 - Ea_2)}{RT}} = e^{\frac{1000}{300}} = 28$

98. rate is given by slow step

99. $\{O_2\}\{O\} = k_{eq}\{O_3\} \Rightarrow \{O\} = k_{eq}\frac{\{O_3\}}{\{O_2\}}$ 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)

$$\begin{array}{llll} & 3A & \rightarrow\ 4B & +\ C \\ t=10 & \frac{3}{5}-x & \frac{4x}{3} & \frac{x}{3} \end{array}$$

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

$$\frac{-d[A]}{dt}=\frac{\frac{3}{5}}{10}\text{atm}/\min^{-1}$$

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)

$$k_1t=\ln\left(\frac{1}{a}\right)$$

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

:

$$k_1=k_2=......$$

$\Rightarrow$ 1st order reaction

6. (C)

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

7. (A)

$$\begin{array}{llll} & A\ \ + & B & \rightarrow\ C \\ t=0 & 3 & 3.2 & - \\ t=t & a-x & 3.2-x & x \\ & =0.6 & =0.8 & =2.4 \end{array}$$

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

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

8. (B)

$[A]_t = 0.3 - 10^{-2} \times 10 = 0.2M$

Zero order reaction

9. (A)

$$\begin{array}{lcccccc} & 2A & \longrightarrow & 3B & + & 4C \\ t=0 & 3 & & - & & - \\ t=t & 3-x & & \frac{3x}{2} & & 2x \end{array}$$

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

At $t = 10\,\text{min}, x = 1.5$

At $t = 20\,\text{min}, x = 3.0$

Rx^n goes to completion and follows $x = kt$

10. (C)

11. (D)

$E_{af} - E_{ab} = \Delta H \Rightarrow E_{ab} = 120\,kJ$

After addition of catalyst.

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

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

12. (D)

13. (A)

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

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

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

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

14. (D)

15. (D)

EXERCISE - 1 [C]

1. (2000)

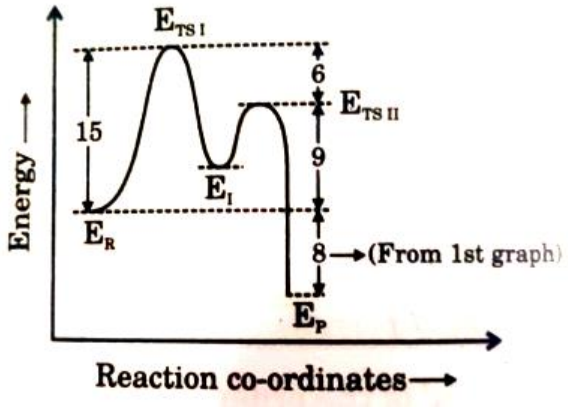
$$k_1 = k_2$$

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

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

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

2. (17)



$$\therefore E_{rsII} - E_P = 17 kJ/mol$$

3. (2571)

$$A(g) \longrightarrow 2B(g) + 3Cl(g)$$

$500 \qquad - \qquad -$

$500 - P \qquad 2P \qquad 3P$

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

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

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

4. (5)

$$nA(g) \longrightarrow An(g)$$

$t = 0 \qquad 2 \qquad -$

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

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

$$\Rightarrow n = 5$$

5. (2)

$$2\times10^{-2}\times1\times100=2\text{kJ}$$

6. (12)

$$\frac{d[C]}{dt}=4\times10^{-3}\times10^{-3}=4\times10^{-6}\,\text{M/min}$$

$$\Rightarrow 4\times10^{-6}\times1\times10\times30\times10^{3}\,\text{cal/min}=1.2\,\text{cal/min}$$

7. (420)

$$A\rightarrow B+C$$

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

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

8. (2)

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

$$\Rightarrow\ \mu=2$$

9. (8)

	A	$+$	B	$\rightarrow$	C	$+$	$\frac{1}{5}D$
t = 0	20		10000		–		–

$$r_A=k[A];\qquad k=\frac{\ln 2}{30}$$

$$P_A\rightarrow a=5;\ P_D\rightarrow b=\frac{10}{5}=2;\ c=1$$

$$a+b+c=8$$

10. (16)

$$k\times8=\ln\left[\frac{1750-1000}{1750-1375}\right]\ \Rightarrow\ t_{1/2}=8,\ t_{3/4}=16$$

PYQ : JEE Main

1. (B)

(b) Given $-\dfrac{d[\mathrm{MnO_4^-}]}{dt} = 4.56 \times 10^{-3}\ \mathrm{Ms^{-1}}$

From the reaction given,

$$-\frac{1}{2}\frac{d[\mathrm{MnO_4^-}]}{dt} = \frac{4.56\times10^{-3}}{2}\mathrm{Ms^{-1}}$$

$$-\frac{1}{2}\frac{d[\mathrm{MnO_4^-}]}{dt} = \frac{1}{5}\frac{d\mathrm{I_2}}{dt}$$

$$\therefore\ -\frac{5}{2}\frac{d[\mathrm{MnO_4^-}]}{dt} = \frac{d\mathrm{I_2}}{dt}$$

On substituting the given value

$$\therefore\ \frac{d\mathrm{I_2}}{dt} = \frac{4.56\times10^{-3}\times5}{2} = 1.14\times10^{-2}\ \mathrm{M/s}$$

2. (D)

(d) For a zero order reaction,

$[\mathrm{A_t}] = [\mathrm{A_0}] - \mathrm{k.t}$

$\Rightarrow\ 0.5 = [\mathrm{A_0}] - 2\times10^{-2}\times25 \Rightarrow [\mathrm{A_0}] = 1\ \mathrm{M}$

3. (B)

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

$\mathrm{E}_a = 150\ \mathrm{kJ/mol}$

For an exothermic reaction,

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

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

4. (D)

(d) From rate law

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

$$\therefore\ -\frac{d[\mathrm{SO_2}]}{dt} = -2\times\frac{d[\mathrm{O_2}]}{dt} = -2\times2.5\times10^{-4}$$

$= -5\times10^{-4}\ \mathrm{mol\ L^{-1}\ s^{-1}}$

5. (C)

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

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

From $T = n \times \mathrm{t}_{1/2}$ $\qquad n = \dfrac{60}{15} = 4$

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

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 = $k[N_2O_5]$

	$2N_2O_5(g) \longrightarrow$	$4NO_2(g) +$	$O_2(g)$
t = 0 min (Pressure in mm Hg)	50	0	0
t = 30 min (Pressure in mm Hg)	$50 - 2p$	$4p$	p

Total pressure $= 50 - 2p + 4p + p = 50 + 3p$

$= 87.5$ mm Hg

$\therefore p = 12.5$ mm Hg

$\therefore p_0 = 50$

$p\,(t = 30\text{ min}) = 50 - 2 \times 12.5 = 25$ for N_2O_5 reactant

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

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

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

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

8. (C)

(c) Rate $= k[A][B] = R$

$R' = k[A][2B]$

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

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

9. (A)

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

If activation energy of the reaction = x

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

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

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)

(d) $H_2O_2\,(aq) \rightarrow H_2O\,(aq) + \frac{1}{2}O_2\,(g)$

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

$$\therefore\ k = \frac{2.303}{50}\log\frac{0.5}{0.125}$$

$$= 2.78 \times 10^{-2}\ \text{min}^{-1}$$

$r = k[H_2O_2] = 2.78 \times 10^{-2} \times 0.05 = 1.386 \times 10^{-3}$ mol min^{-1}

Now

$$-\frac{d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{2d[O_2]}{dt} = k[H_2O_2]$$

$$\therefore\quad \frac{d[O_2]}{dt} = -\frac{1}{2}\times\frac{d[H_2O_2]}{dt}$$

$$= \frac{1.386\times10^{-3}}{2} = 6.93 \times 10^{-4}\ \text{mol min}^{-1}$$

11. (D)

Rate constant is independent of concentration.

12. (A)

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

$$\ln 4 = \frac{E_a}{8.314}\left(\frac{310-300}{310\times300}\right)$$

$$2\ln 2 = \frac{E_a}{8.314}\left(\frac{310-300}{310\times300}\right)$$

$$E_a = \frac{0.693\times2\times8.314\times300\times310}{10} = 107.2\ \text{kJ/mol}$$

13. (B)

(b) $\log\dfrac{k_2}{k_1}=\dfrac{E_a}{2.303R}\left[\dfrac{T_2-T_1}{T_1T_2}\right]$

For reaction A -

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

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

For reaction B -

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

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

From equation (i) and (ii),

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

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

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

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

14. (D)

(d) $k_1=A\cdot e^{-E_{a_1}/RT}$ .....(i)

$k_2=A\cdot e^{-E_{a_2}/RT}$ .....(ii)

On dividing equation (ii) by (i)

$$\Rightarrow \frac{k_2}{k_1}=e^{\frac{(E_{a_1}-E_{a_2})}{RT}}$$

$$\ln\left(\frac{k_2}{k_1}\right)=\frac{E_{a_1}-E_{a_2}}{RT}=\frac{10{,}000}{8.314\times 300}=4$$

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)

(d) $A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$

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

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

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

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

18. (A)

(a) Rate constant of decomposition of $X = 0.05$ μg/year.

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

For zero order kinetics,

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

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

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

19. (C)

(c) $xA \rightarrow yB$

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

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

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

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

$\therefore \quad \frac{x}{y} = 2 \quad \therefore$ 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)

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

21. (A)

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

$$\log\frac{1}{2.5\times10^{-4}} = \frac{E_a}{8.314\times2.303}\left(\frac{1}{600} - \frac{1}{800}\right)$$

$$\Rightarrow \; 3.6 = \frac{E_a}{8.314\times2.303}\times\frac{200}{600\times800} \Rightarrow E_a = 165.4\text{ kJ/mol}$$

22. (D)

(d) Arrhenius equation :

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

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T} \Rightarrow \ln k = \ln A - \left(\frac{E_a}{R\times10^3}\right)\times\frac{10^3}{T}$$

Slope of graph $= \frac{-E_a}{R\times10^3} = \frac{-10}{5}$

$$E_a = 2R\times10^3\text{ J} = 2R\text{ kJ}$$

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)

(d) $2\,H_2(g) + 2\,NO(g) \rightarrow N_2(g) + 2H_2O(g)$

$R_f = K_f[NO]^2\,[H_2]$

This means that, for forward reaction the order of reaction w.r.t. [NO] is 2 and that w.r.t. $[H_2]$ is 1.

Assuming the equilibrium expression,

$$K_{eq} = \frac{[N_2][H_2O]^2}{[H_2]^2[NO]^2} = \frac{K_f}{K_b}$$

$$\Rightarrow K_f\left[NO\right]^2\left[H_2\right] = K_b\frac{\left[N_2\right]\left[H_2O\right]^2}{\left[H_2\right]}$$

At equilibrium, $R_f = R_b \Rightarrow R_b = K_b\dfrac{\left[N_2\right]\left[H_2O\right]^2}{\left[H_2\right]}$

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) $C_t = C_0e^{-kt};\ k = \dfrac{\ln 2}{t_{1/2}}$

$$(C_t)_A = (C_0)_Ae^{-k_At};\ k_A = \frac{\ln 2}{300}$$

$$(C_t)_B = (C_0)_Be^{-k_Bt};\ k_B = \frac{\ln 2}{180}$$

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

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

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

27. (C)

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

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

28. (C)

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

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

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

29. (C)

(c) For Ist order reaction

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

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

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

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

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, $kt = \ln\frac{[A]}{[A_0]}$

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

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

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

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

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

34. (7)

(7) For the first order reaction

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

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

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

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

35. (10)

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

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

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

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

36. (2)

$A \rightarrow$ Products

Rate constant of a first order is given as,

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

37. (45)

(45) ΔH = Energy of products – Energy of reactants

$= Z - (Z + Y) = -45$ kJ/mol

$|\Delta H| = 45$ kJ/mol

38. (47)

(47) Given, $\log K = 20.35 - \dfrac{2.47 \times 10^3}{T}$ ...(i)

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

Comparing equation (i) with equation (ii),

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

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

$= 4\,7293.44$ J/mol $= 47$ 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 Ist 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) $t = \frac{1}{k}\ln\left(\frac{a_0}{a_0 - n}\right)$

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

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

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

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

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

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

Given, $A_0 = B_0$ 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) $t_{1/2} \propto \frac{1}{[P_0]^{n-1}}$

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

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

48. (225)

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

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

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

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

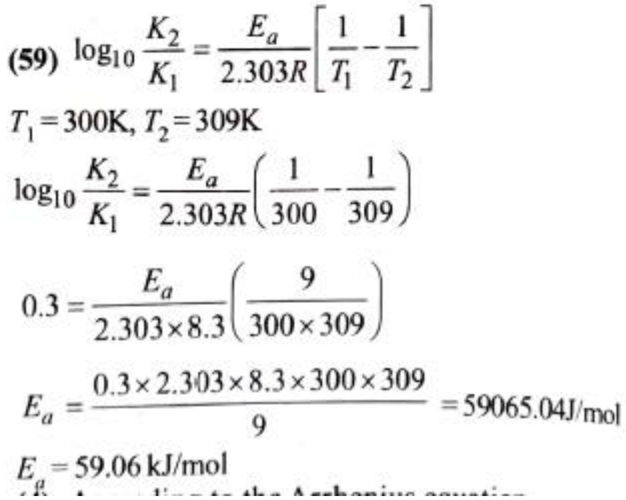
$$\Rightarrow -19.3 = -\frac{10^3}{T\times 2.3} \Rightarrow \quad T = 225\times 10^{-1}\,\text{K}$$

49. (216)

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

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

50. (59)



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

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

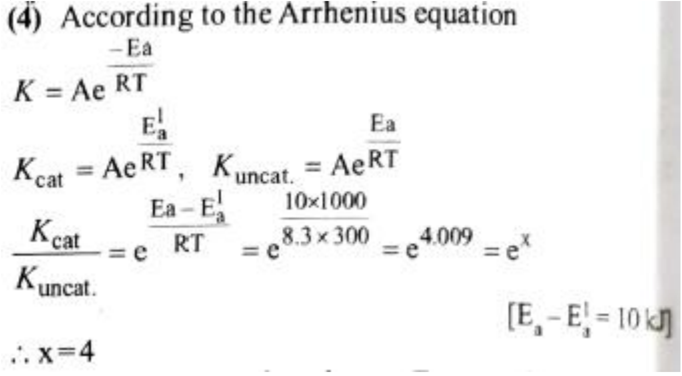
$$\log_{10}\frac{K_2}{K_1}=\frac{E_a}{2.303R}\left(\frac{1}{300}-\frac{1}{309}\right)$$

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

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

$E_a=59.06$ kJ/mol

51. (4)



(4) According to the Arrhenius equation

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

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

$$\frac{K_{cat}}{K_{uncat.}}=e^{\frac{Ea-E_a^l}{RT}}=e^{\frac{10\times1000}{8.3\times300}}=e^{4.009}=e^{x}$$

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

$\therefore x=4$