

Foundation Builder (Objective)

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

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

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

4. relative strength \propto rate constant

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

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

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

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

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

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

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

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

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

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 1st 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 1st order is 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 & $t_{1/2} \propto \{H^+\}$ so, $r = k \{sugar\}^1 \{H^+\}^0$

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

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

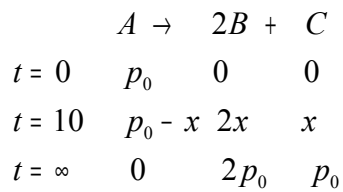
58. rate is independent on conc.

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

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

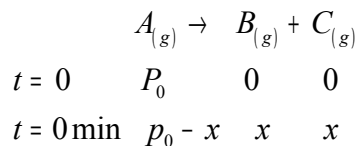
62. As per theory

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

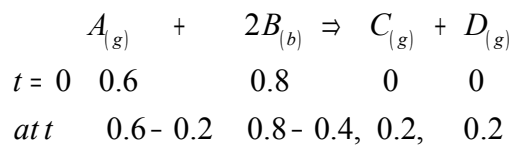
66.



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

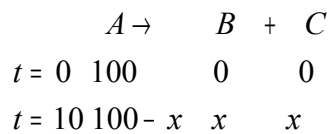
$$k = \frac{2.303}{10} \log\left(\frac{P_0}{r_0 - x}\right)$$

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. 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

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

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

Foundation Builder (Subjective)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 Δx ; $10M$)

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. 1st 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. 1st 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. $t_{99.9\%} = \frac{2.303}{K} \log \left(\frac{100}{100 - 99g} \right) = \frac{6.9}{k} = 10 \times \frac{0.69}{k} = 10t_{1/2}$

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

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

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

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

18.

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

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

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

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

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

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

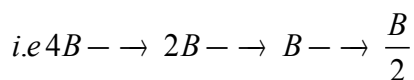
$$\frac{\{A_t\}}{\{A_0\}} = 0.0526$$

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

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

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

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



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

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

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

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

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

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

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

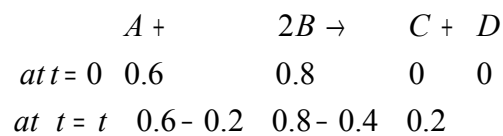
$$t_{1/2} \propto a, \quad n=0$$

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

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

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

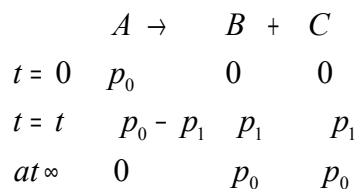
36.



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

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

37.

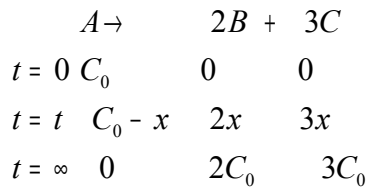


$$p_3 = p_{\infty} \quad p_{\infty} = 2p_0 \Rightarrow p_0 = \frac{p_{\infty}}{2} = \frac{p_3}{2}$$

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

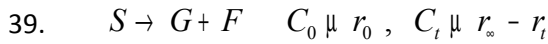
$$k = \frac{2.303}{t} \log \left(\frac{p_0}{p_0 - p_1} \right) = \frac{2.303}{t} \log \left(\frac{p_{\infty}}{p_{\infty} - p_2} \right) = \frac{1}{t} \ln \left(\frac{p_3}{p_3 - p_2} \right)$$

38.

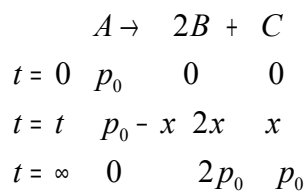


At time t $V_2 = C_0 + 4x$ $x = \frac{V_2 - C_0}{4}$ at ∞ $V_3 = 5C_0$

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



40.

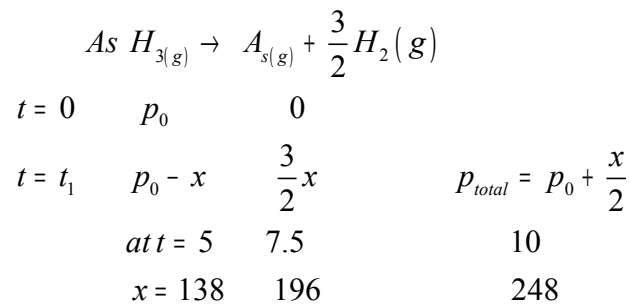


At 10 min $176 = p_0 + 2x$ $270 = 3p_0 \Rightarrow p_0 = 90$ $x = 43$

(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.

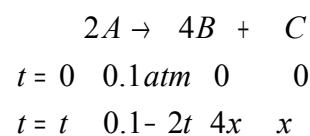


$$k = \frac{2.303}{t} \log \frac{\{A_0\}}{\{A_t\}} = \frac{2.303}{t} \log \left(\frac{p_0}{p_0 - x} \right)$$

if will be same for all value of x

42. As above

43.

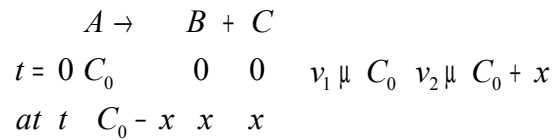


$$P_{\text{total}} = 0.1 + 3x = 0.145 \quad x = 0.015$$

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

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

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

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

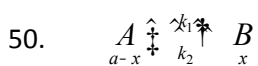
$$k = k_1 + k_2 + \dots k_n$$

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

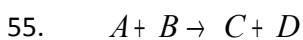
$$E_a = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \log_e \left(\frac{k_2}{k_1} \right) = 10.22 \text{ kcal/mol}$$

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) ΔH ; 20 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) step 1 \rightarrow 1, step = 2

Get equipped for IIT-JEE

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 1st 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

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

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

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

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

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

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

7. for $A \rightarrow$ product

for $2R \rightarrow$ Product

3 half life in 60 min

$$4 - \frac{1st}{20min} \rightarrow 2 - \frac{2nd}{40min} \rightarrow 1$$

$$4 - \frac{1st}{20min} \rightarrow 2 - \frac{2nd}{20} \rightarrow 1 - \frac{3rd}{20} \rightarrow 0.5$$

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

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

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

$$A \rightarrow B + C$$

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

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

9. 1st 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. $k_1 = \frac{0.693}{(t_{1/2})_1}, k_2 = \frac{0.693}{(t_{1/2})_2} \quad Ea = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \left(\frac{k_2}{k_1} \right)$

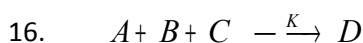
12. $e^{-Ea/RT} = 3.8 \times 10^{-18} \quad (as \% = 3.8 \times 10^{-16})$

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

13. As per theory

14. As derived in theory

15. as per theory



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

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

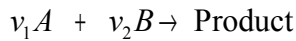
$$\mu \{C\}^1 \{B\}^1 \Rightarrow \text{rate} = k \{B\} \{C\} \quad \text{order} = 1 + 1 = 2$$

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

26. (A) $5^1 \Rightarrow$ for 1st order (C) rate = constant

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

28. As per theory

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

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

30. As per theory 31. As per theory

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

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

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

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

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

35. $k = Ae^{-Ea/RT}$ k only T dependent

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

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

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

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

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

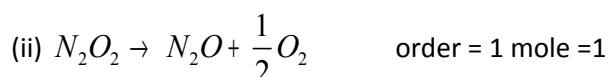
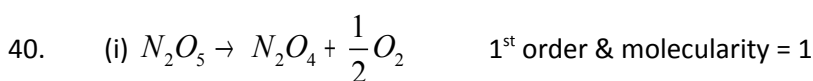
$$k = Ae^{-Ea/RT} \Rightarrow \log \frac{k_1}{k_2} = \frac{Ea}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

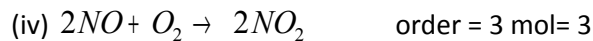
$$t_{99.9\%} = \frac{2.303}{K} \log \left(\frac{100}{100 - 99.9} \right) = \frac{6.93}{k} = 10t_{1/2}$$

38. As per theory

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

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





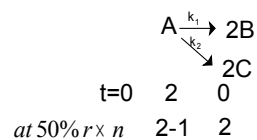
41, 42. Slower step is r.d.s

43. $rate = k\{O\}\{O_3\}$ from 1st r × n $k_{eq} = \frac{\{O_2\}\{O\}}{\{O_3\}}$

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

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

47 & 48



At 50% total moles = 1+2 = 3

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

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

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

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

Order = 2 + 1 = 3

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

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

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

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

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

53. $Ea_f - Ea_b = \Delta H$

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

$n=5$

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

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

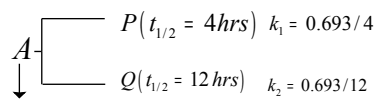
57. $a_t = \frac{a_0}{2^{\left(\frac{t}{t_{1/2}}\right)}}$



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

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

60.



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