Foundation Builder (Objective)

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

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

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

14. as per theory

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

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

23. as question number 22

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

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

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

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

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

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

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

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

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. $\left(t_{1/2}\right)_{zeroth} = \frac{\{A_0\}}{2k_0}$ ...(1) $\left(t_{1/2}\right)_{1^{st}} = \frac{0.693}{k_1}$ ...(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 = $\frac{1}{k}$ $a - x = \frac{a}{e}$

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

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

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

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

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

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

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

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

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

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 $P_0 + 2x = 176 \Rightarrow x = 43$

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

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.

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

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

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

67.

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

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

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

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

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

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

93. as rate µ $\{A\}\{B\}$ 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 µ $\{O\}\{O_3\}$ µ $\frac{\{O_3\}^2}{\{O_2\}}$

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

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

Foundation Builder (Subjective)

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

(a) $\frac{\Delta\{N_2\}}{\Delta t} = 10^{-4} mol\, l^{-1} S^{-1}$ (b) $\frac{\Delta[H_2]}{\Delta t} = 3 \times 10^{-4} Ms^{-1}$

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

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

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

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

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

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

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

rate $\mu \{A\}^2 \quad rate \to \frac{1}{9} times$

(b) $A \to \frac{2}{3}A$ rate $\to \frac{4}{9}$ times

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

8. (a) $if\ k_1C >> 1 \quad \frac{dC}{dt} = \frac{k_1}{k_2}$ order = 0

(b) if $k_2C << 1 \quad \frac{dc}{dt};\ k_1C$ order = 1

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

(ii) $A \to 2A$ & $B \to 2B$ $\quad rate \Rightarrow 8\,\text{times}$

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

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

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

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

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

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

13. 1 hour $\Rightarrow 75\%$

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

14. 1st order $75\% \to 72\,\text{min}\quad 50\% \to 36\,\text{min}$

(i) $36\,\text{min}$

(ii) $A \xrightarrow{t_{1/2}} \frac{A}{2} \xrightarrow{t_{1/2}} \frac{A}{4} \xrightarrow{t_{1/2}} \frac{A}{8}\quad 3t_{1/2} \to\ for\ 87.5$ 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 $\Rightarrow\ t_{1/2}$ = constant

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

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

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

18.

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

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

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

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

$$t = 166.16\min$$

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

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

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

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

(ii) $n_{N_2O} \approx \dfrac{6.2}{12} = 0.1\,mol \approx 2.2176\,lit$

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

$$i.e\, 4B \longrightarrow 2B \longrightarrow B \longrightarrow \frac{B}{2}$$

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

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

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

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

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

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

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

rate = $k\{A_t\} = 3.43\times10^{-3}Ms^{-1}$

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

28. $t = \dfrac{2.303}{3.3\times10^{-4}}\log\left(\dfrac{100}{60}\right)$; 26 min

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

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

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

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

(C) $k = 4.88\times10^6,\ rate = 1.21\times10^{-2}Ms^{-1}$

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

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

order = 1+ 2 = 3

(B) $rate = k\{NO\}^2\{Cl_2\}$ (C) $k = \dfrac{1\times10^{-3}}{(0.05)^2(0.05)} = 8\ L^2mol^{-2}s^{-1}$

. (D) $rate = 8\times0.2\times(0.4)^2 = 0.256\,Ms^{-1}$

31. It is zero order

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

$k = \dfrac{\Delta p}{\Delta t} = \dfrac{(4-3.5)\times10^3}{100}\,pa/s$

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

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

33. $0.12 \xrightarrow[10\,hours]{t_{1/2}} 0.06 \xrightarrow[10\,hours]{t_{1/2}} 0.03$

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

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

34. Reaction 1

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

Reaction 2

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

Reaction 3

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

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

rate = $\{A\}$

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

36.

$$\begin{array}{lllll} & A + & 2B \rightarrow & C + & D \\ at\, t = 0 & 0.6 & 0.8 & 0 & 0 \\ at\ \ t = t & 0.6 - 0.2 & 0.8 - 0.4 & 0.2 & \end{array}$$

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

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

37.

$$\begin{array}{llll} & A \rightarrow & B\ + & C \\ t = 0 & p_0 & 0 & 0 \\ t = t & p_0 - p_1 & p_1 & p_1 \\ at\, \infty & 0 & p_0 & p_0 \end{array}$$

$$p_3 = p_\infty \quad p_\infty = 2p_0 \Rightarrow \quad p_0 = p_{\frac{\infty}{2}} = p_{\frac{3}{2}}$$

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

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

38.

$$
\begin{array}{llll}
 & A \rightarrow & 2B + & 3C \\
t = 0 & C_0 & 0 & 0 \\
t = t & C_0 - x & 2x & 3x \\
t = \infty & 0 & 2C_0 & 3C_0
\end{array}
$$

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

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

39. $S \rightarrow G + F \quad C_0 \propto r_0\ ,\ C_t \propto r_\infty - r_t$

40.

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

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

$$
\begin{array}{llll}
 & AsH_{3(g)} \rightarrow & A_{s(g)} + \frac{3}{2}H_2(g) & \\
t = 0 & p_0 & 0 & \\
t = t_1 & p_0 - x & \frac{3}{2}x & p_{total} = p_0 + \frac{x}{2} \\
 & at\, t = 5 & 7.5 & 10 \\
 & x = 138 & 196 & 248
\end{array}
$$

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

if will be same for all value of x

42. As above

43.

$$
\begin{array}{llll}
 & 2A \rightarrow & 4B + & C \\
t = 0 & 0.1\,atm & 0 & 0 \\
t = t & 0.1 - 2t & 4x & x
\end{array}
$$

P_{total} = 0.1 + 3x = 0.145 x= 0.015

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

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

44.

$$\begin{array}{lllll} & A \rightarrow & B & + & C \\ t = 0 & C_0 & 0 & & 0 \\ at\ t & C_0 - x & x & & x \end{array} \quad v_1 \propto C_0 \quad v_2 \propto C_0 + x$$

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

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

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

$$k = k_1 + k_2 + ...k_n$$

(b) yes,

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

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

49. As per theory

50. $\underset{a-x}{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{x}{B}$

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

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

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

51. $E_a = 104.5\,kJ/mol$

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

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

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

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

52. $Ea = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\ln\left(\frac{k_2}{k_1}\right) = 55.32\,kJ/mol$

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

$E_a = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\log_e\left(\frac{k_2}{k_1}\right) = 10.22\,kcal/mol$

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

Vont haff equation

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

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

55. $A + B \rightarrow C + D$

$E_f - E_b = \Delta H$, $E_b = 85 - 20 = 65\,kJ/mol$

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

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

(d) as $E_a \rightarrow decreas \quad k \rightarrow \; increase$

60. $E_a = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\ln\left(\frac{K_2}{K_1}\right)$

61. $\frac{K_1}{K_2} = e^{\frac{-(Ea_1 - Ea_2)}{RT}}$

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

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

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

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

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

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

$= k_1k_2\{NO\}^2\{H_2\}$

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

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

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

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

w.r.t B is 0

rate = $k\{A\}$

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

2. As it is 1st order $r \times n$

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

3.
$$\begin{array}{llll} & C_2H_4O \rightarrow & CH_4 + & CO \\ t = 0 & 80 & 0 & 0 \\ at\,t = 20 & 80 - x & x & x \end{array}$$

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

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

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

$E_a = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\ln\left(\frac{k_2}{k_{11}}\right)$

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

So in 4th $r \times n$ $\Delta H = -40\,k\,cal$

7. $for\ A \rightarrow$ prodcut

3 half life in 60 min

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

$t_{1/2} = const$

for $2R \rightarrow$ Product

$4 \xrightarrow[20\min]{1st} 2 \xrightarrow[40\min]{2nd} 1$

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

only $2t_{\frac{1}{2}}$ in 60 min

8.

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

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

9. 1st order overall

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

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

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

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

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

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

13. As per theory

14. As derived in theory

15. as per theory

16. $$A + B + C \xrightarrow{K} D$$

$$\propto \left\{ B \right\}^1$$

Rate $\propto \left\{ A \right\}^0$

$$\propto \left\{ C \right\}^1 \left\{ B \right\}^1 \Rightarrow \quad rate = k\left\{ B \right\}\left\{ C \right\} \quad order = 1 + 1 = 2$$

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

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

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

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

$v_1 A + v_2 B \rightarrow \text{Product}$

$t = 0 \quad \{A\}_0 \quad \{B_0\}$

$at\ t \quad \{A\}_0 - v_1 x$

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

$\Rightarrow \int_0^x \frac{dx}{\{A\}_0 - v_1 x} = k_1 \int_0^t dt$ k $\Rightarrow v_1 \frac{1}{v_1} \ln\left(\frac{\{A\}_0}{\{A_0\} - v_1 x}\right) = k_1 t$

20. C_A is independent on R, k_2 & S

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

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

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

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

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) $5^1 \Rightarrow$ $for\ 1^{st}\ order$ (C) rate = constant

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

28. As per theory

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

$A = 10^5$, $Ea = 2000 R \times 2.303 = 9.152 k\,cal$

30. As per theory 31. As per theory

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

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

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

Rate µ $\{2n\}$, $rate$µ $\left\{H^+\right\}^2\ as\ pH \to 3 - 2\,rate \to 100\,time$

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

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

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

(B) $t_{15/16} = t_{(1-1/24)}$ means after $4t_{1/2}\ or\ 2t_{3/4}$

(C) $t_{31/32} = t_{(1-1/25)} = 5t_{1/2}$

(D) $t_{255/256} = t_{\left(1-\frac{1}{28}\right)} = 2t_{\left(1-\frac{1}{24}\right)} = 2t_{15/16}$

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

$k = Ae^{-Ea/RT} \Rightarrow \log\frac{k_1}{k_2} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

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

38. As per theory

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

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

40. (i) $N_2O_5 \to N_2O_4 + \frac{1}{2}O_2$ 1st order & molecularity = 1

(ii) $N_2O_2 \to N_2O + \frac{1}{2}O_2$ order = 1 mole =1

(iii) $2HI \to H_2 + I_2$ order = 2 molecular =2

(iv) $2NO + O_2 \rightarrow 2NO_2$ order = 3 mol= 3

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

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

$\{O\} = k_{eq}\frac{\{O_3\}}{\{O_2\}}$ 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

$A \xrightarrow{k_1} 2B$, $A \xrightarrow{k_2} 2C$

t=0 2 0

$at\ 50\%\ r \times n$ 2-1 2

At 50% total moles = 1+2 = 3

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

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

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

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

Order = 2 + 1 = 3

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

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

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

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

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

53. $Ea_f - Ea_b = \Delta H$

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

n=5

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

$\propto \{B\}$

56. $t_{1/2} \propto \dfrac{1}{a^3}$ t = $\dfrac{1}{a^{n-1}}$ x = 4

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

58. $A \rightarrow P \qquad t_{1/2} = 2hr$

$B \rightarrow Q \qquad t_{1/2} = 8hr$

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

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

60.

$A \rightarrow P(t_{1/2} = 4hrs) \quad k_1 = 0.693/4$

$A \rightarrow Q(t_{1/2} = 12\,hrs) \quad k_2 = 0.693/12$

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