SOLUTIONS

EXERCISE #O-I

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RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

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

4. $-\frac{d[A]}{4dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{2}\frac{d[D]}{dt}$

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

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

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

$\because \quad \log\frac{x}{y} = 0.3$

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

6. Rate = slope = $\frac{10}{20}$ = 0.5 M sec^{-1}

7. 'k' depends only upon temperature and catalyst.

8. $\frac{k_1'}{2} = \frac{k_1''}{2} = \frac{k_1}{1} = \frac{k}{2}$

9. Rate = k $[A]^1$ $[B]^0$

10. Rate = k $[A]^1$ $[B]^2$

Initial Rate $= 1 \times 10^{-2} = k \times 1 \times 1^2$

$K = 10^{-2}$

$\therefore$ Final Rate $= kc\,[A]^1\,[B]^1$

$= 10^{-2} \times 0.5 \times 0.5^2$

$= 1.25 \times 10^{-3}$ M sec^{-1}

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11. $-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = 1.5 \times 10^{-4}$

$\therefore \quad -\frac{d[NO_2]}{dt} = 3 \times 10^{-4} = 3 \times 10^{-3}[NO_2]^2$

$[NO_2] = 0.316$ M

ZERO ORDER REACTIONS

13. $[A]_t = [A]_0 - kt$

$[A]_0 = [A]_t + kt$

$= 0.05 + 0.2 \times \frac{30}{60}$

$= 0.15$ M

14. $[B]_t = 2\ kt$

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

$= 0.2$ M

15. For zero order reaction

Rate = k

16. $t_{1/2} = \frac{[A]_0}{2k}$

$\log(t_{1/2}) = \log [A]_0 - \log(2k)$

FIRST ORDER, SECOND ORDER & n^{th} ORDER REACTIONS

19. Rate = k [A]

20. Rate = $4 \times 10^{-3} \times 0.02$

$= 8 \times 10^{-5}$ M sec^{-1}

21. $k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t}$

$= \frac{1}{20}\ell n\left(\frac{1}{0.25}\right)$

$= 0.06931$ min^{-1}

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22. $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 10^{-2}\ sec^{-1}$

Rate = $k \times [A] = 10^{-2} \times 0.1 = 10^{-3}$ M sec^{-1}

23. Fraction of reactant left after n half lift = $\left(\frac{1}{2}\right)^n$

$\because$ 40 min is 2 half life

$\therefore \quad \frac{a_t}{a_o} = \left(\frac{1}{2}\right)^2 = \frac{1}{4}$

24. $t_{1/2} = \frac{0.693}{1.155\times10^{-3}} = 600$ sec.

26. $k = \frac{k_1}{k_2} = \frac{[D]^2}{[P]} \ln\left(\frac{1}{0.6}\right) = 0.0255$

$t = \frac{1}{0.0225} \ell n \left(\frac{0.6}{0.36}\right) = 20$ min.

27. $k = \frac{1}{100} \ln\left(\frac{100}{100-75}\right) = \frac{2\ln 2}{100}$

$t = \frac{1}{k} \ln\left(\frac{200}{200-150}\right) c = 100$ min.

28. $k = \frac{1}{20} \ln\left(\frac{100}{100-80}\right) = 0.0805$

$t_{1/2} = \frac{0.693}{0.0805} = 8.66$ min.

30. Rate = $k[A]_t = k\,[A]_0\, e^{-kt}$

31. | Slope | = k $= \frac{2}{10} \times 2.303\ min^{-1} = \frac{2\times2.303}{10\times60}\ sec^{-1} = 7.7 \times 10^{-3}\ sec^{-1}$

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second order reaction

33. $\frac{1}{a_t} = \frac{1}{a_o} + kt$

34. $t_{1/2} = \frac{0.693}{8\times10^{-5}}$ min $= 8.6625 \times 10^3$ min.

nth order and pseudo order reaction

37. $A \longrightarrow nB$

A_0 **0**

$A_0 - x$ nx

At intersection point [A] = [B] $\Rightarrow A_0 - x = nx \Rightarrow x = \frac{A_0}{n+1}$

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

38. For n^{th} order reaction

$t_{1/2} \times \frac{1}{a_o^{n-1}} = \frac{c}{a_o^{n-1}}$

$\log(t_{1/2}) = \log c - (n-1) = \log a_0$

$\because$ Slope $= -(n-1) = -1$

$\therefore$ $n = 2$

40. Concentration of A remain constant because it is present in large amount so order w.r.t. A will be zero in overall order or reaction.

41. $t_{1/2} \propto \frac{1}{[A]_0} \propto [A]_0^{-1}$

On comparing with

$t_{1/2} \propto [A]_0^{1-n}$

$1 - n = -1 \Rightarrow n = 2$

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Experimental determination of order

42. $r = K[A]^x[B]^y$

from exp. 1 and 2 on increasing $[A]_0$ 2 times rate becomes 8 time, so x = 3

from exp. 2 and 4 on increasing $[B]_0$ 2 times rate does not change, so y = 0

$r = K[A]^3[B]^0$

43. $r = k[A]^x[B]^y$

from exp 1 Q 2 x = 1

from exp 2 Q 3 y = 0

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

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

$6.93\times10^{-6} = k\times 0.01$

$k = 6.93\times10^{-4}$

$t_{1/2} = \frac{0.693}{6.93\times10^{-4}} = 1000$ sec

t = 50 min = 3000 sec

$[A]_t = \frac{[A]_0}{2^3} = \frac{0.5}{8} = \frac{1}{16}$ M

$r = 6.93\times10^{-4}\times\frac{1}{16}$ M sec^{-1}

44. $t_{1/2} \propto P_0^{1-n}$

$\frac{950}{235} = \left(\frac{250}{500}\right)^{1-n}$

$\log\frac{950}{235} = (1-n)\log\frac{1}{2}$

$0.6 = -(1-n)\times0.3$

$1-n = -2 \Rightarrow n = 3$

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Experimental determination of First order rate constant

45. $A \longrightarrow 2B + C$

$t = 0$	P_o	0	0
$t = t$	$P_o - x$	$2x$	x
$t = \infty$	0	$2P_o$	P_o

$3P_o = 270 \Rightarrow P_o = 90$

$P_t = P_0 + 2x = 176 \Rightarrow 2x = 80 \Rightarrow x = 43$

$(P_A)_t = P_o - x = 90 - 43 = 47$

46. $(CH_3)_2.CHN{=}NCH(CH_3)_2(g) \longrightarrow N_2(g) + C_6H_{10}(g)$

$t = 0$	P_o	0	0
$t = t$	$P_o - x$	x	x

$P_t = P_o + x \Rightarrow x = P_t - P_o$

$P_o - x = P_o - (P_t - P_o) = 2P_o - P_t$

$$k = \frac{1}{t}\ln\frac{P_o}{P_o - x} = \frac{1}{t}\ln\frac{P_o}{2P_o - P_t}$$

47. $H_2O_2(aq) \longrightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$

$t = 0$	C	0	0
$t = t$	$C - x$	x	$\frac{x}{2}$
$t = \infty$	0	C	$\frac{C}{2}$

$\frac{C}{2} \propto 50$ and $\frac{x}{2} \propto 5$

$$k = \frac{1}{20}\ln\frac{C}{C - x} = \frac{1}{20}\ln\frac{50}{45}$$

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48. $NH_4NO_2(aq) \longrightarrow N_2(g) + 2H_2O(\ell)$

$t = 0$	C	0	0
$t = t$	C–x	x	2x
$t = \infty$	0	C	2C

$C \propto 70$ and $x \propto 40$

$$k = \frac{1}{t} \ln \frac{70}{30}$$

49. $A \longrightarrow B + C$

$$K = \frac{1}{t}\ln\frac{r_\infty - r_0}{r_\infty - r_t} = \frac{1}{10}\ln\frac{100-0}{100-50} = \frac{1}{10}\ln 2 = 0.0693 \text{ min}^{-1}$$

50. $K = \dfrac{1}{t}\ln\dfrac{r_\infty - r_0}{r_\infty - r_t}$

$$= \frac{1}{10}\ln\frac{-10-40}{-10-15}$$

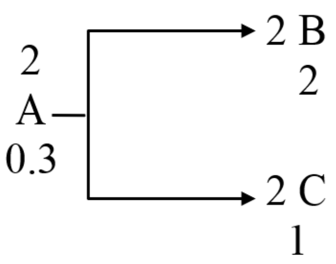
$$\frac{1}{10}\ln\frac{50}{25}$$

0.0693 sec

parallel first order reaction

51. $\dfrac{[B]}{[C]} = \dfrac{k_1}{k_2}$

52.



$\because \quad \dfrac{[B]}{[C]} = \dfrac{k_1}{k_2} = \dfrac{1}{2}$

Total moles = 0.5 + 2 + 1 = 3.5

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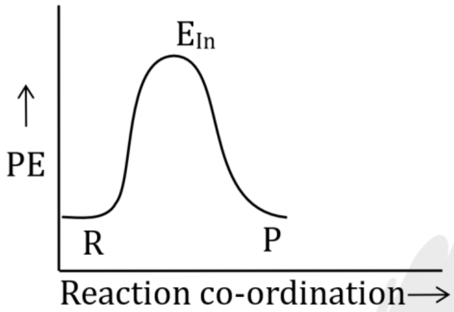
Collison Theory

53. $r = Z_{11}.e^{-Ea/RT}.P$

55. 

56. Molecules with sufficient amount of energy and proper orientation

Effect of temperature on rate

58. $k = A\, e^{-Ea/RT}$

59. $k = A$ if $T \to \infty$.

60. $k = A$ if $T \to \infty$.

61. $\ell n\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

62. $\ell n\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

63. Fraction of molecules = $e^{-Ea/RT} = \frac{3.8\times10^{-16}}{100}$

64. % of activated molecules= $e^{-Ea/RT}\times100$

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65. The reaction which has more steep curve will be more temp sensitive.

66. $\ell n\, k = \ell n\, A - \frac{Ea}{R}\left(\frac{1}{T}\right)$

Effect of catalyst on rate

68. Slope = $-\frac{Ea}{R} = -\frac{8.3 \times 1000}{8.3} = -1000$

mechanism of reaction

70. Rate - k [A] [B]

71. Rate = $k_3\,[Q]^2\,[P]$

$\because K_{eq} = \frac{k_1}{k_2} = \frac{[Q]^2}{[P]}$

$\therefore [Q]^2 = \frac{k_1}{k_2}\,[P]$

$\therefore$ Rate = $\frac{k_1}{k_2} k_3\,[P]^2$