Ch 15 Chemical Kinetics

27) a) $R = \frac{-\Delta[A]}{2\Delta t} = \frac{-\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$

b) $\frac{-(-0.100\ M/s)}{2} = \frac{-\Delta[B]}{\Delta t}$ $\quad \frac{\Delta[B]}{\Delta t} = -0.0500\ M/s$

$\frac{-(-0.100\ M/s)}{2} = \frac{-\Delta[C]}{3\Delta t}$ $\quad \frac{\Delta[C]}{\Delta t} = 0.150\ M/s$

31) a) $R = \frac{-(0.913 - 1.000\ M)}{10. - 0\ s} = 0.0087\ M/s$ $\quad R = \frac{-(0.637 - 0.697\ M)}{(50. - 40.\ s)} = 0.0060\ M/s$

$R = -\frac{\Delta[C_4H_8]}{\Delta t}$

reaction slows as conc of reactant ↓

33) a)(i) $R = \frac{-\Delta[Br_2]}{\Delta t} = \frac{0.75M - 1.00M}{25 - 0\ s} = 0.010\ M/s$ $\quad$ tangents

ii → 35s, 0.68M $\quad$ 15s, 0.85M

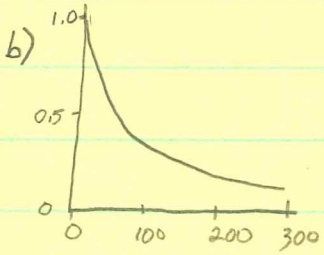
iii → 60.s, 0.53M $\quad$ 40.s, 0.66M

ii) slope $= \frac{0.68 - 0.85M}{35 - 15s} = -0.0085\ M/s$

iii) slope $= \frac{0.53 - 0.66M}{60. - 40.\ s} = -0.0065\ M/s = \frac{\Delta[Br_2]}{\Delta t} = \frac{\Delta[HBr]}{2\Delta t}$ $\quad \frac{\Delta[HBr]}{\Delta t} = 0.013\ M/s$

35) a) $R \propto [A]$ 1st order

b)



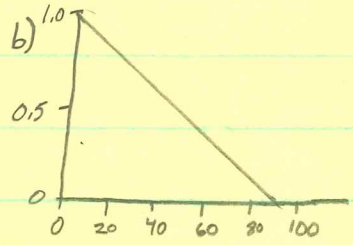
c) $Rate = k[A]$ $\quad$ values from graph in text

$0.002\ M/s = k[0.2M]$ $\quad k = 0.01\ s^{-1}$

or slope $= \frac{0.010 - 0\ M/s}{1.0 - 0.0\ M} = 0.010\ s^{-1} = k$

36) a) R does not depend on [A] → 0 order

b)



c) $Rate = k[A]^0$

$Rate = k$

$Rate = 0.011\ M/s$

37) a) $R = k[A]$ $\quad M/s = k\ M$ $\quad k = s^{-1}$

b) $R = k[A]^2$ $\quad M/s = k\ M^2$ $\quad k = M^{-1}s^{-1}$

c) $R = k[A]^0$ $\quad M/s = k$

39) a) $R = k[A]^1[B]^2[C]^0 = k[A][B]^2$ b) 3rd (1+2)

c) $\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k(2[A])[B]^2}{k[A][B]^2} = 2$ (R will ↑2x since rxn is 1st order in A)

d) $\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[A](2[B])^2}{k[A][B]^2} = 4$ (R will ↑4x since rxn is 2nd order in B)

e) No change since rxn is Ø order in [C]

f) $\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k(2[A])(2[B])^2}{k[A][B]^2} = 8$ (R ↑2x for A + 4x for B)

45) $\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[NO_2]^m[F_2]^n}{k[NO_2]^m[F_2]^n}$ $\frac{0.051}{0.026} = \frac{k(0.200)^m(0.100)^n}{k(0.100)^m(0.100)^n}$ $1.96 = 2^m$ $m = 1$

$\frac{0.103}{0.051} = \frac{k(0.200)^m(0.200)^n}{k(0.200)^m(0.100)^n}$ $2.01 = 2^n$ $n = 1$

By inspection: When $[NO_2]$ is 2x and $[F_2]$ const R ↑2x → 1st order

When $[F_2]$ is 2x and $[NO_2]$ const R ↑2x → 1st order

47) a) zero order R does not depend on [ ] b) 1st order $t_{1/2} = \frac{0.693}{k}$ no dependence on conc

c) 2nd order $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

55) a) $t_{1/2} = \frac{0.693}{1.42\times10^{-4}\,s^{-1}} = 4880\,s$

b) $\ln[A]_t = -kt + \ln[A]_0$ $-kt = \ln[A]_t - \ln[A]_0$ $t = \frac{\ln\frac{[A]_t}{[A]_0}}{-k}$

$t = \ln\frac{0.25[SO_2Cl_2]}{[SO_2Cl_2]} = \frac{\ln(0.25)}{-1.42\times10^{-4}\,s^{-1}} = 9800\,s$

c) $t = \frac{\ln\left(\frac{0.78}{1.00}\right)}{-1.42\times10^{-4}\,s^{-1}} = 1700\,s$

d) $\ln[SO_2Cl_2]_t = -k(200.5) + \ln(0.150)$

$\ln[\ ] = -1.9255$

$[SO_2Cl_2]_{200} = e^{-1.9255} = 0.146M$

$[SO_2Cl_2]_{500} = e^{-1.968} = 0.140M$

63) $\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$ $\text{slope} = -\frac{E_a}{R}$ $E_a = -\text{slope}\,R$

$E_a = -(-7445K)\left(\frac{8.314\,J}{K\cdot mol}\right)\left(\frac{1kJ}{1000\,J}\right) = 61.90\,kJ/mol$

73) "a" reactants are symmetrical (higher chance for correct orientation)

77)

a) $Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Cl$ fast

$Cl + CHCl_3 \xrightarrow{k_3} HCl + CCl_3$ slow

$Cl + CCl_3 \xrightarrow{k_4} CCl_4$ fast

$Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$

b) intermediates Cl, CCl_3

c) $R = k_3[Cl][CHCl_3]$

$k_1[Cl_2] = k_2[Cl]^2$ $\quad [Cl] = \sqrt{\frac{k_1[Cl_2]}{k_2}} = \frac{k_1}{k_2}[Cl_2]^{1/2}$

$R = k[Cl_2]^{1/2}[CHCl_3]$

78) a) $NO_2 + Cl_2 \xrightarrow{k_1} ClNO_2 + Cl$ slow

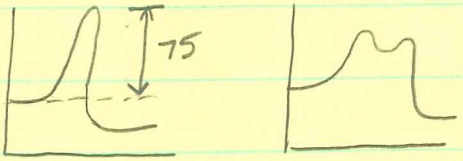
$NO_2 + Cl \xrightarrow{k_2} ClNO_2$ fast

$2NO_2 + Cl_2 \rightarrow 2ClNO_2$

b) Cl $\quad$ c) $R = k_1[NO_2][Cl_2]$

79) Need greater surface area for catalysis to occur at active sites

80)

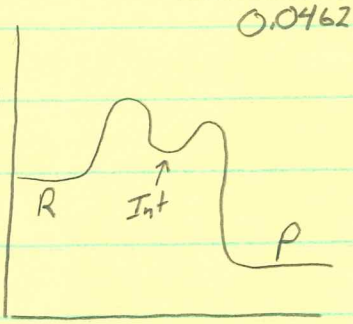


83) $t_{1/2}$ is constant 15 hr $\rightarrow$ 1st order $\quad t_{1/2}^{a+b}$

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{15.0\,hr} = 0.0462\,hr^{-1}$

83c) $t = \frac{\ln\left(\frac{0.10[CH_3CN]_0}{[CH_3CN]_0}\right)}{0.0462\,hr^{-1}}$ $\quad t = 49.8\,hr$

95) b)



a) 2 steps $\quad$ c) 1st step is limiting - higher Ea

d) overall exo $\quad R > P$

96) a) 1st step higher Ea $\quad$ b) $R = k[HCl][H_2C{=}CH_2]$ 2nd order overall

c) exo overall