Chapter 21 Homework Solutions

21.1 2 A + B $\rightarrow$ 2 C + 3 D $\quad \frac{d[C]}{dt} = 2.7\,Ms^{-1}$

$$Rate = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2}\left(2.7\,Ms^{-1}\right) = 1.35\,Ms^{-1}$$

$$Rate = 1.35\,Ms^{-1} = -\frac{1}{2}\frac{d[A]}{dt} \rightarrow \frac{d[A]}{dt} = -2(1.35\,Ms^{-1}) = -2.7\,Ms^{-1}$$

$$Rate = 1.35\,Ms^{-1} = -\frac{d[B]}{dt} \rightarrow \frac{d[B]}{dt} = -1(1.35\,Ms^{-1}) = -1.35\,Ms^{-1}$$

$$Rate = 1.35\,Ms^{-1} = +\frac{1}{3}\frac{d[D]}{dt} \rightarrow \frac{d[D]}{dt} = +3(1.35\,Ms^{-1}) = +4.05\,Ms^{-1}$$

21.2 Compare Expts. 1 and 2: $\frac{r_{o2}}{r_{o1}} = \left(\frac{[A]_{o2}}{[A]_{o1}}\right)^x \rightarrow \frac{2.83}{8.50} = \left(\frac{0.3}{0.1}\right)^x \rightarrow 0.333 = (3.0)^x$

x = ln(0.333)/ln(3.0) = -1.10/+1.10= -1

Compare Expts. 2 and 3: $\frac{r_{o3}}{r_{o2}} = \left(\frac{[B]_{o3}}{[B]_{o2}}\right)^y \rightarrow \frac{7.80}{2.83} = \left(\frac{3.0}{2.0}\right)^y \rightarrow 2.76 = (1.5)^y$

y = ln(2.76)/ln(1.5) = 1.02/0.41= 2.50 = 5/2

$$r_o = k[A]_o^x[B]_o^y = k\frac{[B]_o^{5/2}}{[A]_o}$$

$$k = r_o\frac{[A]_o}{[B]_o^{5/2}} = 8.50\,Ms^{-1}\frac{0.10\,M}{\left(2.0\,M\right)^{5/2}} = 0.15\,M^{-1/2}s^{-1}$$

We used experiment 1 to calculate k. One gets the same answer using either of the other two experiments.

21.3 $\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{[A]_{o1}}{[A]_{o2}}\right)^{n-1} = \left(\frac{p_{01}}{p_{02}}\right)^{n-1}$

Note: The ratio of concentrations is the same as the ratio of pressures.

$\frac{880\,s}{410\,s} = \left(\frac{363\,torr}{169\,torr}\right)^{n-1} \rightarrow 2.15 = \left(2.15\right)^{n-1} \rightarrow$ n-1 = 1 $\rightarrow$ n = 2

21.4 $\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{[A]_{o1}}{[A]_{o2}}\right)^{x-1} \rightarrow \frac{50}{200} = \left(\frac{0.4}{0.2}\right)^{x-1} \rightarrow 0.25 = (2.0)^{x-1}$

Therefore, $x - 1 = \frac{\ln(0.25)}{\ln(2.0)} = \frac{-1.386}{+0.693} = -2.0 \rightarrow$ x = -2+1 = -1

21.5 $\dfrac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\dfrac{[A]_{o1}}{[A]_{o2}}\right)^{x-1} \rightarrow \dfrac{126}{200} = \left(\dfrac{0.1}{0.25}\right)^{x-1} \rightarrow 0.63 = (0.40)^{x-1}$

Therefore, $x - 1 = \dfrac{\ln(0.63)}{\ln(0.40)} = \dfrac{-0.462}{-0.916} = +0.5 = +1/2 \rightarrow$ x = 1/2+1 = 3/2

21.6 (a) $[A]_o$ = 1.30 M, [A] = 0.50(1.30 M) = 0.65 M at t = $t_{1/2}$ = 42 s

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \rightarrow k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A]_o}\right) = \frac{1}{42\,s}\left(\frac{1}{0.65\,M} - \frac{1}{1.30\,M}\right) = 0.0183\,M^{-1}s^{-1}$$

Note: you will get the same answer if you use the formula for the half-life of a second-order reaction, $k = 1/(t_{1/2}[A]_o)$

(b) $[A]_o$ = 1.30 M, [A] = ? at t = 60 s

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \rightarrow \frac{1}{[A]} = \frac{1}{[A]_o} + kt = \frac{1}{1.30\,M} + (0.0183\,M^{-1}s^{-1})(60\,s) = 1.867\,M^{-1}$$

$$[A] = \frac{1}{1.867\,M^{-1}} = 0.54\,M$$

(c) $[A]_o$ = 1.30 M, [A] = 0.80 M at t = ?

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \rightarrow t = \frac{1}{k}\left(\frac{1}{[A]} - \frac{1}{[A]_o}\right) = \frac{1}{0.0183\,M^{-1}s^{-1}}\left(\frac{1}{0.80\,M} - \frac{1}{1.30\,M}\right) = 26.3\,s$$

21.7 Preliminary (Integrated Rate Equation)

$$\frac{d[A]}{dt} = -k[A]^3 \rightarrow \int_{[A]_0}^{[A]} \frac{1}{[A]^3} d[A] = \int_0^t -kdt$$

$$\int_{[A]_0}^{[A]} [A]^{-3} d[A] = \int_0^t -kdt \rightarrow \frac{1}{(-3+1)}\left\{[A^{-2}]\right\}_{[A]_0}^{[A]} = -k(t-0)$$

$$\frac{1}{2}\left\{\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right\} = +kt \rightarrow \left\{\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right\} = +2kt$$

(a) $[A]_0$ = 0.80 M , [A] = 0.50 M , t = 6.4 s

$$k = \frac{1}{2t}\left\{\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right\} = \frac{1}{2(6.4\,s)}\left\{\left(\frac{1}{0.50\,M}\right)^2 - \left(\frac{1}{0.80\,M}\right)^2\right\} = 0.190\,M^{-2}s^{-1}$$

(b) $[A]_0 = 0.80$ M , t = 20 s , k = 0.19 $M^{-2}s^{-1}$, [A] = ?

$$\frac{1}{[A]^2} = \frac{1}{[A]_0^2} + 2kt = \frac{1}{(0.80\,M)^2} = 2(0.19\,M^{-2}s^{-1})(20\,s) = 9.163\,M^{-2}$$

$$\frac{1}{[A]} = (9.1625\,M^{-2})^{1/2} = 3.027\,M^{-1}$$

$$[A] = \frac{1}{3.027\,M^{-1}} = 0.33\,M$$

(c) $[A]_0 = 0.80$ M , [A] = 0.30 M , k = 0.19 $M^{-2}s^{-1}$ t = ?

$$t = \frac{1}{2k}\left\{\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right\} = \frac{1}{2(0.19\,M^{-2}s^{-1})}\left\{\left(\frac{1}{0.30\,M}\right)^2 - \left(\frac{1}{0.80\,M}\right)^2\right\} = 25.1\,s \approx 25\,s$$

21.8 Preliminary (Integrated Rate Equation)

$$\frac{d[A]}{dt} = -k[A]^{3/2} \rightarrow \frac{d[A]}{[A]^{3/2}} = [A]^{-3/2}d[A] = -kdt$$

$$\int_{[A]_o}^{[A]} [A]^{-3/2}d[A] = -k\int_0^t dt$$

$$\left[-2[A]^{-1/2}\right]_{[A]_o}^{[A]} = -kt \rightarrow -2\left(\frac{1}{[A]^{1/2}} - \frac{1}{[A]_o^{1/2}}\right) = -kt$$

$$\frac{1}{[A]^{1/2}} - \frac{1}{[A]_o^{1/2}} = \frac{1}{2}kt \quad \text{or} \quad \frac{1}{[A]^{1/2}} = \frac{1}{[A]_o^{1/2}} + \frac{1}{2}kt$$

(a) $t = t_{1/2}$ when $[A]=[A]_o/2$.
k = 0.03 $M^{-1/2}s^{-1}$, $[A]_0 = 0.50$ M , [A] = 0.50(0.50 M) = 0.25 M , t = ?

$$\frac{1}{[A]^{1/2}} = \frac{1}{[A]_o^{1/2}} + \frac{1}{2}kt \rightarrow t = \left(\frac{2}{k}\right)\left\{\frac{1}{[A]^{1/2}} - \frac{1}{[A]_o^{1/2}}\right\}$$

$$t_{1/2} = \left(\frac{2}{0.03\,M^{-1/2}s^{-1}}\right)\left\{\frac{1}{[0.25\,M]^{1/2}} - \frac{1}{[0.50\,M]^{1/2}}\right\} = 39\,s$$

(b) k = 0.03 $M^{-1/2}s^{-1}$, $[A]_0 = 0.50$ M , t = 25 s ,[A] = ?

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$$\frac{1}{[A]^{1/2}} = \frac{1}{[A]_o^{1/2}} + \frac{1}{2}kt = \frac{1}{(0.5\,M)^{1/2}} + \frac{1}{2}(0.03\,M^{-1}s^{-1})(25\,s) = 1.78\,M^{-1/2}$$

$$[A]^{1/2} = \frac{1}{1.78\,M^{-1/2}} = 0.562\,M^{1/2} \rightarrow [A] = (0.562\,M^{1/2})^2 = 0.315\,M \approx 0.32\,M$$

(c) $k = 0.03\ M^{-1/2}s^{-1}$, $[A]_0 = 0.50$ M , $[A] = 0.20$ M , t = ?

$$t = \frac{2}{k}\left(\frac{1}{[A]^{1/2}} - \frac{1}{[A]_o^{1/2}}\right) = \frac{2}{0.03M^{-1/2}s^{-1}}\left(\frac{1}{(0.2M)^{1/2}} - \frac{1}{(0.5M)^{1/2}}\right) = 54.8\,s \approx 55\,s$$

21.9 (a) $[B]_\infty = 0.90$ M

$[A]_\infty + [B]_\infty = [A]_o \rightarrow [A]_\infty = [A]_o - [B]_\infty = 1.20\text{ M} - 0.90\text{ M} = 0.30\text{ M}$

$$\frac{k_1}{k_2} = \frac{[B]_\infty}{[C]_\infty} = \frac{0.90}{0.30} = 3.00$$

(b) $$\frac{k_1}{k_2} = 3.00 \rightarrow k_2 = \frac{k_1}{3.00} = \frac{0.60\,s^{-1}}{3.00} = 0.20\,s^{-1}$$

$$[C] = \frac{k_2}{k_1 + k_2}[A]_o\left\{1 - e^{-(k_1+k_2)t}\right\} = \frac{0.20}{0.60 + 0.20}(1.20\,M)\left\{1 - e^{-(0.60+0.20)(2.0)}\right\} = 0.24\,M$$

21.10 $k_1 = 1.5x10^{-3}\ s^{-1}$ at $T_1 = 40\ ^oC = 313$ K and $k_2 = 8.6x10^{-2}\ s^{-1}$ at $T_2 = 80\ ^oC = 353$ K.

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

$$E_a = -(8.31\,J/mol\cdot K)\frac{\ln\left(8.6x10^{-2}/1.5x10^{-3}\right)}{\left[\frac{1}{353K} - \frac{1}{313K}\right]} = 9.29x10^4\ J/mol \approx 93\,kJ/mol$$

$$\ln(k_1) = \ln(A) - \frac{E_a}{RT_1} \rightarrow \ln(A) = \ln(k_1) + \frac{E_a}{RT_1}$$

$$\ln(A) = \ln(1.5x10^{-3}) + \frac{9.29x10^4}{(8.31)(313)} = 29.21 \quad \rightarrow \quad A = e^{29.21} = 4.9x10^{12}\ s^{-1}$$

(b) $k_1 = 1.5x10^{-3}\ s^{-1}$ at $T_1 = 40\ ^oC = 313$ K , k_3 = ? at $T_3 = 130\ ^oC = 403$K

$$\ln(k_3/k_1) = -\frac{E_a}{R}\left[\frac{1}{T_3} - \frac{1}{T_1}\right] = -\frac{9.29x10^4}{8.31}\left[\frac{1}{403} - \frac{1}{313}\right] = 7.98$$

$$\frac{k_3}{1.5x10^{-3}} = e^{7.98} = 2922 \quad \rightarrow \quad k_3 = 4.38\text{ s} \approx 4.4\text{ s}$$

(c) $k_4 = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{200\,s} = 3.47x10^{-3}\,s^{-1}$

$k_1 = 1.5x10^{-3}\ s^{-1}$ at $T_1 = 40\ ^oC = 313$ K , $k_4 = 3.47x10^{-3}\ s^{-1}$ at T_4 = ?

$$\ln\left(k_4 / k_1\right) = -\frac{E_a}{R}\left[\frac{1}{T_4} - \frac{1}{T_1}\right] \rightarrow \quad \frac{1}{T_4} = \frac{1}{T_1} - \frac{R}{E_a}\ln(k_4 / k_1)$$

$$\frac{1}{T_4} = \frac{1}{313} - \frac{8.31}{9.29x10^4}\ln(3.47x10^{-3} / 1.5x10^{-3}) = 3.120x10^{-3}\,K^{-1}$$

$$T_4 = \frac{1}{3.120x10^{-3}\,K^{-1}} = 321\,K - 273 = 48\,^oC$$

21.11 **ΔH‡:** $Slope = -5450 = -\frac{\Delta H^{\pm}}{R}$

$$\Delta H^{\pm} = -R(-5450\,K) = (-8.31\,J / mol \cdot K)(-5450\,K) = +4.53x10^4\ J / mol = 45.3\,kJ / mol$$

ΔS‡: $Int = \ln\left(R/_{N_A h}\right) + \frac{\Delta S^{\pm}}{R} \rightarrow \frac{\Delta S^{\pm}}{R} = Int - \ln\left(R/_{N_A h}\right)$

$$\frac{\Delta S^{\pm}}{R} = 12.80 - \ln\left(2.1x10^{10}\right) = -10.97$$

$$\Delta S^{\pm} = -10.15R = (-10.97)(8.31\,J / mol \cdot K) = -91.2\,J / mol \cdot K$$

21.12 $\ln(k) = \ln\left[CT^{1/2}e^{-E_o/_{RT}}\right] = \ln(C) + \frac{1}{2}\ln(T) - \frac{E_o}{RT}$

$$\frac{d\ln(k)}{dT} = \frac{E_a}{RT^2} = 0 + \frac{1}{2T} + \frac{E_o}{RT^2}$$

$$E_a = RT^2\left(0 + \frac{1}{2T} + \frac{E_o}{RT^2}\right) = \frac{1}{2}RT + E_o$$

21.13 Part (a) Pre-Equilibrium: $A_2 \underset{}{\overset{K}{\rightleftarrows}} A + A$

Followed by RDS: $A + B \xrightarrow{k} P$

From Pre-Equilibrium: $K = \frac{[A]^2}{[A_2]} \rightarrow [A] = K^{1/2}[A_2]^{1/2}$

$$Rate = \frac{d[P]}{dt} = k[A][B] = k\left(K^{1/2}[A_2]^{1/2}\right)[B] = kK^{1/2}[A_2]^{1/2}[B] = k_{eff}[A_2]^{1/2}[B]$$

21.14 Steady-State Approximation on [AB]

$$\frac{\Delta[AB]}{\Delta t} = 0 = k_1[A][B] - k_{-1}[AB] - k_2[AB][A] = k_1[A][B] - [AB]\left\{k_{-1} + k_2[A]\right\}$$

$$\text{Therefore } [AB] = \frac{k_1[A][B]}{k_{-1} + k_2[A]}$$

$$Rate = \frac{\Delta[P]}{\Delta t} = k_2[AB][A] = k_2\left\{\frac{k_1[A][B]}{k_{-1} + k_2[A]}\right\}[A]$$

$$Rate = \frac{\Delta[P]}{\Delta t} = \frac{k_1 k_2[A]^2[B]}{k_{-1} + k_2[A]}$$

21.15 A $\rightarrow$ 2 B + C $\Phi_R = 2.1x10^2 = 210$

$$n_A = 2.28\, mmol\ B \cdot \frac{10^{-3}\ mol\ B}{1\, mmol\ B} = 2.28x10^{-3}\ mol\ B \cdot \frac{1 mol\ A}{2\, mol\ B} = 1.14x10^{-3}\ mol\ A$$

$$\Phi_R = \frac{n_A}{n_{ph}} \ \rightarrow\ n_{ph} = \frac{n_A}{\Phi_R} = \frac{1.14x10^{-3}\ mol}{210} = 5.43x10^{-6}\ mol\ ph$$

$$N_{ph} = 5.43x10^{-6}\ mol\ ph \cdot \frac{6.02x10^{23}\ ph}{1 mol\ ph} = 3.3x10^{18}\ ph$$

21.16 $E_{tot} = (100\, J/s)(45 \min)(60\, s/\min) = 2.70x10^5\ J$

$$E_{ph} = \frac{hc}{\lambda(m)} = \frac{1.99x10^{-25}\ J/m}{\lambda(m)} = \frac{1.99x10^{-25}\ J/m}{490x10^{-9}\ m} = 4.06x10^{-19}\ J$$

$$n_{ph}(incident) = \frac{E_{tot}}{E_{ph}} \cdot \frac{1 mol}{N_A\ ph} = \frac{2.70x10^5\ J}{4.06x10^{-19}\ J/ph} \cdot \frac{1 mol}{6.02x10^{23}\ ph} = 1.105\, mol$$

$$n_{ph}(absorbed) = n_{ph} = 1.105\, mol \cdot f_{abs} = 1.105\, mol \cdot \left(1 - f_{trans}\right)$$

$$= 1.105\, mol \cdot (1 - 0.40) = 0.663\, mol$$

$$\Phi_R = \frac{n_{React}}{n_{ph}(abs)} = \frac{0.344}{0.663} = 0.52$$

21.17 τ_0 = 6.0 ns = 6.0x10^{-9} s k_Q = 3.0x10^{8} L/mol-s = 3.0x10^{8} M^{-1}s^{-1}

A 60% reduction in fluorescence quantum yield means that:

$$\frac{\Phi_F}{\Phi_{F,0}} = 1.00 - 0.60 = 0.40 \quad \rightarrow \quad \frac{\Phi_{F,0}}{\Phi_F} = 2.50$$

$$\frac{\Phi_{F,0}}{\Phi_F} = 1 + \tau_0 k_Q [Q] \quad \rightarrow \quad [Q] = \frac{\frac{\Phi_{F,0}}{\Phi_F} - 1}{\tau_0 k_Q} = \frac{2.50 - 1}{(6.0x10^{-9}\ s)(3.0x10^{8}\ M^{-1}s^{-1})} = 0.83M$$

(Illustrative Note: an 80% reduction, for example would correspond to:

$$\frac{\Phi_F}{\Phi_{F,0}} = 0.20 \quad \rightarrow \quad \frac{\Phi_{F,0}}{\Phi_F} = 5.0)$$

21.18 (a) $\ln\left[\frac{I_F}{I_{F,0}}\right] = -t/\tau_0 \quad \rightarrow \quad \ln(0.65) = \frac{-35\,ns}{\tau_0} \quad \rightarrow \quad \tau_0 = \frac{-35\,ns}{-0.43} = 81\,ns$

(b) $\Phi_F = \frac{k_F}{k_0} = k_F \tau_0 = (4.8x10^{6}\ s^{-1})(81x10^{-9}\ s) = 0.40$

21.19 $(v_o)_1$ = 3.7x10^{-8} M/s when $[S]_1$ = 2.5x10^{-4} M $[E]_o$ = 4.0x10^{-6} M
$(v_o)_2$ = 9.8x10^{-8} M/s when $[S]_2$ = 1.0x10^{-3} M

$$v_o = \frac{V_m[S]}{K_M + [S]} \quad \rightarrow \quad \frac{1}{v_o} = \frac{K_M + [S]}{V_M[S]} = \frac{K_M}{V_M}\frac{1}{[S]} + \frac{1}{V_m} = slope \cdot \frac{1}{[S]} + Int$$

$$slope = \frac{K_M}{V_m} \quad and \quad Int = \frac{1}{V_m}$$

$$slope = \frac{\frac{1}{(v_o)_2} - \frac{1}{(v_o)_1}}{\frac{1}{[S]_2} - \frac{1}{[S]_1}} = \frac{\frac{1}{9.8x10^{-8}\ M/s} - \frac{1}{3.7x10^{-8}\ M/s}}{\frac{1}{1.0x10^{-3}\ M} - \frac{1}{2.5x10^{-4}\ M}} = 5.61x10^{3}\ s$$

$$Int = \frac{1}{(v_o)_1} - slope \cdot \frac{1}{[S]_1} = \frac{1}{3.7x10^{-8}\ M/s} - (5.61x10^{3}\ s) \cdot \frac{1}{2.5x10^{-4}\ M} = 4.59x10^{6}\ s/M$$

$$V_m = \frac{1}{Int} = \frac{1}{4.59x10^6\ s/M} = 2.18x10^{-7}\ M/s$$

$$K_M = slope \cdot V_m = (5.61x10^3\ s)(2.18x10^{-7}\ M/s) = 1.22x10^{-3}\ M$$

$$V_m = k_2[E]_o \quad \rightarrow \quad k_2 = \frac{V_m}{[E]_o} = \frac{2.18x10^{-7}\ M/s}{4.0x10^{-6}\ M} = 5.45x10^{-2}\ s^{-1}$$

21.20 $$\frac{1}{v_o} = \frac{K_M + [S]}{V_M[S]} = \frac{K_M}{V_M}\frac{1}{[S]} + \frac{1}{V_m} = slope \cdot \frac{1}{[S]} + Int$$

(a) $\text{Slope} = \frac{\text{K}_\text{M}}{\text{V}_\text{m}} = \frac{20\,\text{mM}}{80\,\text{mM/s}} = 0.25\,\text{s}$

(b) $\text{Int} = \frac{1}{\text{V}_\text{m}} = \frac{1}{80\,\text{mM/s}} = 0.0125\,\text{s/mM} \approx 0.013\,\text{s/mM}$

(c) $\text{V}_\text{m} = \text{k}_2\left[\text{E}\right]_\text{o} \quad \text{®} \quad \text{k}_2 = \frac{\text{V}_\text{m}}{[\text{E}]_\text{o}} = \frac{80\,\text{mM/s}}{2\,\text{mM}} = 40\,\text{s}^{-1}$