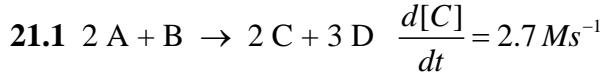


Chapter 21 Homework Solutions

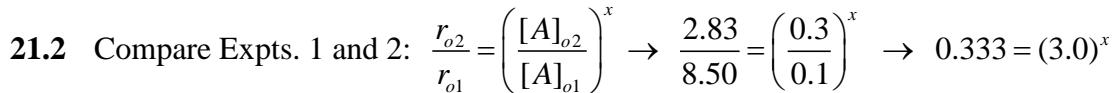


$$\text{Rate} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{2} (2.7 \text{ Ms}^{-1}) = 1.35 \text{ Ms}^{-1}$$

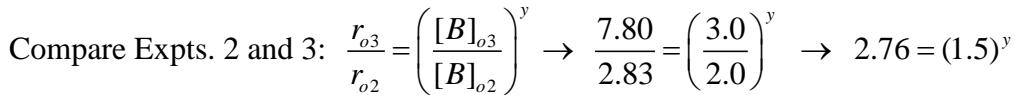
$$\text{Rate} = 1.35 \text{ Ms}^{-1} = -\frac{1}{2} \frac{d[A]}{dt} \rightarrow \frac{d[A]}{dt} = -2(1.35 \text{ Ms}^{-1}) = -2.7 \text{ Ms}^{-1}$$

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

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



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

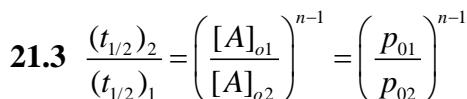


$$y = \ln(2.76)/\ln(1.5) = 1.02/0.41 = 2.50 = 5/2$$

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

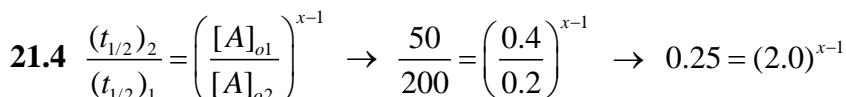
$$k = r_o \frac{[A]_o}{[B]_o^{5/2}} = 8.50 \text{ Ms}^{-1} \frac{0.10 M}{(2.0 M)^{5/2}} = 0.15 M^{-1/2} s^{-1}$$

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



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

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



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

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

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

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

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

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) $[A]_o = 1.30 \text{ M}$, $[A] = ?$ at $t = 60 \text{ s}$

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

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

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

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

21.7 Preliminary (Integrated Rate Equation)

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

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

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

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

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

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

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

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

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

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

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

21.8 Preliminary (Integrated Rate Equation)

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

$$\int_{[A]_0}^{[A]} [A]^{-3/2} d[A] = -k \int_0^t dt$$

$$[-2[A]^{-1/2}]_{[A]_0}^{[A]} = -kt \rightarrow -2 \left(\frac{1}{[A]^{1/2}} - \frac{1}{[A]_0^{1/2}} \right) = -kt$$

$$\frac{1}{[A]^{1/2}} - \frac{1}{[A]_0^{1/2}} = \frac{1}{2} kt \quad \text{or} \quad \frac{1}{[A]^{1/2}} = \frac{1}{[A]_0^{1/2}} + \frac{1}{2} kt$$

$$(a) t = t_{1/2} \text{ when } [A] = [A]_0/2.$$

$$k = 0.03 \text{ M}^{-1/2}\text{s}^{-1}, [A]_0 = 0.50 \text{ M}, [A] = 0.50(0.50 \text{ M}) = 0.25 \text{ M}, t = ?$$

$$\frac{1}{[A]^{1/2}} = \frac{1}{[A]_0^{1/2}} + \frac{1}{2} kt \rightarrow t = \left(\frac{2}{k} \right) \left\{ \frac{1}{[A]^{1/2}} - \frac{1}{[A]_0^{1/2}} \right\}$$

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

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

$$\frac{1}{[A]^{1/2}} = \frac{1}{[A]_0^{1/2}} + \frac{1}{2} kt = \frac{1}{(0.5 \text{ M})^{1/2}} + \frac{1}{2}(0.03 \text{ M}^{-1}\text{s}^{-1})(25 \text{ s}) = 1.78 \text{ M}^{-1/2}$$

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

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

$$t = \frac{2}{k} \left(\frac{1}{[A]^{1/2}} - \frac{1}{[A]_0^{1/2}} \right) = \frac{2}{0.03 M^{-1/2} s^{-1}} \left(\frac{1}{(0.2 M)^{1/2}} - \frac{1}{(0.5 M)^{1/2}} \right) = 54.8 s \approx 55 s$$

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

$$[A]_\infty + [B]_\infty = [A]_0 \rightarrow [A]_\infty = [A]_0 - [B]_\infty = 1.20 \text{ M} - 0.90 \text{ M} = 0.30 \text{ M}$$

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

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

$$[C] = \frac{k_2}{k_1 + k_2} [A]_0 \left\{ 1 - e^{-(k_1 + k_2)t} \right\} = \frac{0.20}{0.60 + 0.20} (1.20 \text{ M}) \left\{ 1 - e^{-(0.60 + 0.20)(2.0)} \right\} = 0.24 \text{ M}$$

21.10 $k_1 = 1.5 \times 10^{-3} \text{ s}^{-1}$ at $T_1 = 40 \text{ }^\circ\text{C} = 313 \text{ K}$ and $k_2 = 8.6 \times 10^{-2} \text{ s}^{-1}$ at $T_2 = 80 \text{ }^\circ\text{C} = 353 \text{ K}$.

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

$$E_a = -(8.31 \text{ J/mol} \cdot \text{K}) \frac{\ln(8.6 \times 10^{-2} / 1.5 \times 10^{-3})}{\left[\frac{1}{353 \text{ K}} - \frac{1}{313 \text{ K}} \right]} = 9.29 \times 10^4 \text{ J/mol} \approx 93 \text{ kJ/mol}$$

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

$$\ln(A) = \ln(1.5 \times 10^{-3}) + \frac{9.29 \times 10^4}{(8.31)(313)} = 29.21 \rightarrow A = e^{29.21} = 4.9 \times 10^{12} \text{ s}^{-1}$$

(b) $k_1 = 1.5 \times 10^{-3} \text{ s}^{-1}$ at $T_1 = 40 \text{ }^\circ\text{C} = 313 \text{ K}$, $k_3 = ?$ at $T_3 = 130 \text{ }^\circ\text{C} = 403 \text{ K}$

$$\ln(k_3/k_1) = -\frac{E_a}{R} \left[\frac{1}{T_3} - \frac{1}{T_1} \right] = -\frac{9.29 \times 10^4}{8.31} \left[\frac{1}{403} - \frac{1}{313} \right] = 7.98$$

$$\frac{k_3}{1.5 \times 10^{-3}} = e^{7.98} = 2922 \rightarrow k_3 = 4.38 \text{ s} \approx 4.4 \text{ s}$$

$$(c) \ k_4 = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{200 \text{ s}} = 3.47 \times 10^{-3} \text{ s}^{-1}$$

$k_1 = 1.5 \times 10^{-3} \text{ s}^{-1}$ at $T_1 = 40 \text{ }^\circ\text{C} = 313 \text{ K}$, $k_4 = 3.47 \times 10^{-3} \text{ s}^{-1}$ at $T_4 = ?$

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

$$\frac{1}{T_4} = \frac{1}{313} - \frac{8.31}{9.29 \times 10^4} \ln(3.47 \times 10^{-3} / 1.5 \times 10^{-3}) = 3.120 \times 10^{-3} \text{ K}^{-1}$$

$$T_4 = \frac{1}{3.120 \times 10^{-3} \text{ K}^{-1}} = 321 \text{ K} - 273 = 48 \text{ }^\circ\text{C}$$

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

$$\Delta H^\ddagger = -R(-5450 \text{ K}) = (-8.31 \text{ J/mol} \cdot \text{K})(-5450 \text{ K}) = +4.53 \times 10^4 \text{ J/mol} = 45.3 \text{ kJ/mol}$$

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

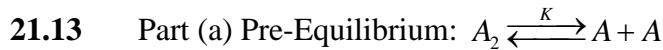
$$\frac{\Delta S^\ddagger}{R} = 12.80 - \ln(2.1 \times 10^{10}) = -10.97$$

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

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

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

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



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

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

21.14 Steady-State Approximation on [AB]

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

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 $A \rightarrow 2 B + C$ $\Phi_R = 2.1 \times 10^2 = 210$

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

$$\Phi_R = \frac{n_A}{n_{ph}} \rightarrow n_{ph} = \frac{n_A}{\Phi_R} = \frac{1.14 \times 10^{-3} \text{ mol}}{210} = 5.43 \times 10^{-6} \text{ mol ph}$$

$$N_{ph} = 5.43 \times 10^{-6} \text{ mol ph} \cdot \frac{6.02 \times 10^{23} \text{ ph}}{1 \text{ mol ph}} = 3.3 \times 10^{18} \text{ ph}$$

21.16 $E_{tot} = (100 \text{ J / s})(45 \text{ min})(60 \text{ s / min}) = 2.70 \times 10^5 \text{ J}$

$$E_{ph} = \frac{hc}{\lambda(m)} = \frac{1.99 \times 10^{-25} \text{ J / m}}{\lambda(m)} = \frac{1.99 \times 10^{-25} \text{ J / m}}{490 \times 10^{-9} \text{ m}} = 4.06 \times 10^{-19} \text{ J}$$

$$n_{ph}(\text{incident}) = \frac{E_{tot}}{E_{ph}} \cdot \frac{1 \text{ mol}}{N_A \text{ ph}} = \frac{2.70 \times 10^5 \text{ J}}{4.06 \times 10^{-19} \text{ J / ph}} \cdot \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ ph}} = 1.105 \text{ mol}$$

$$\begin{aligned} n_{ph}(\text{absorbed}) &= n_{ph} = 1.105 \text{ mol} \cdot f_{abs} = 1.105 \text{ mol} \cdot (1 - f_{trans}) \\ &= 1.105 \text{ mol} \cdot (1 - 0.40) = 0.663 \text{ mol} \end{aligned}$$

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

$$21.17 \quad \tau_0 = 6.0 \text{ ns} = 6.0 \times 10^{-9} \text{ s} \quad k_Q = 3.0 \times 10^8 \text{ L/mol-s} = 3.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$$

A 60% reduction in fluorescence quantum yield means that:

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

$$\frac{\Phi_{F,0}}{\Phi_F} = 1 + \tau_0 k_Q [Q] \rightarrow [Q] = \frac{\frac{\Phi_{F,0}}{\Phi_F} - 1}{\tau_0 k_Q} = \frac{2.50 - 1}{(6.0 \times 10^{-9} \text{ s})(3.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1})} = 0.83 \text{ M}$$

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

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

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

$$(\text{b}) \quad \Phi_F = \frac{k_F}{k_0} = k_F \tau_0 = (4.8 \times 10^6 \text{ s}^{-1})(81 \times 10^{-9} \text{ s}) = 0.40$$

$$21.19 \quad (v_o)_1 = 3.7 \times 10^{-8} \text{ M/s} \quad \text{when } [S]_1 = 2.5 \times 10^{-4} \text{ M} \quad [E]_o = 4.0 \times 10^{-6} \text{ M}$$

$$(v_o)_2 = 9.8 \times 10^{-8} \text{ M/s} \quad \text{when } [S]_2 = 1.0 \times 10^{-3} \text{ M}$$

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

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

$$\text{slope} = \frac{\frac{1}{(v_o)_2} - \frac{1}{(v_o)_1}}{\frac{1}{[S]_2} - \frac{1}{[S]_1}} = \frac{\frac{1}{9.8 \times 10^{-8} \text{ M/s}} - \frac{1}{3.7 \times 10^{-8} \text{ M/s}}}{\frac{1}{1.0 \times 10^{-3} \text{ M}} - \frac{1}{2.5 \times 10^{-4} \text{ M}}} = 5.61 \times 10^3 \text{ s}$$

$$\text{Int} = \frac{1}{(v_o)_1} - \text{slope} \cdot \frac{1}{[S]_1} = \frac{1}{3.7 \times 10^{-8} \text{ M/s}} - (5.61 \times 10^3 \text{ s}) \cdot \frac{1}{2.5 \times 10^{-4} \text{ M}} = 4.59 \times 10^6 \text{ s/M}$$

$$V_m = \frac{1}{Int} = \frac{1}{4.59 \times 10^6 \text{ s/M}} = 2.18 \times 10^{-7} \text{ M/s}$$

$$K_M = slope \cdot V_m = (5.61 \times 10^3 \text{ s})(2.18 \times 10^{-7} \text{ M/s}) = 1.22 \times 10^{-3} \text{ M}$$

$$V_m = k_2 [E]_o \rightarrow k_2 = \frac{V_m}{[E]_o} = \frac{2.18 \times 10^{-7} \text{ M/s}}{4.0 \times 10^{-6} \text{ M}} = 5.45 \times 10^{-2} \text{ s}^{-1}$$

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) Slope = $\frac{K_M}{V_m} = \frac{20 \text{ mM}}{80 \text{ mM/s}} = 0.25 \text{ s}$

(b) Int = $\frac{1}{V_m} = \frac{1}{80 \text{ mM/s}} = 0.0125 \text{ s/mM} \approx 0.013 \text{ s/mM}$

(c) $V_m = k_2 [E]_o$ \textcircled{R} $k_2 = \frac{V_m}{[E]_o} = \frac{80 \text{ mM/s}}{2 \text{ mM}} = 40 \text{ s}^{-1}$