

22. $0.0120/0.0080 = 1.5$; Reactant B is used up 1.5 times faster than reactant A. This corresponds to a 3 to 2 mol ratio between B and A in the balanced equation. $0.0160/0.0080 = 2$; Product C is produced twice as fast as reactant A is used up. So the coefficient for C is twice the coefficient for A. A possible balanced equation is: $2A + 3B \rightarrow 4C$

24. $\text{Rate} = k[\text{Cl}]^{1/2}[\text{CHCl}_3]$, $\frac{\text{mol}}{\text{L s}} = k \left(\frac{\text{mol}}{\text{L}} \right)^{1/2} \left(\frac{\text{mol}}{\text{L}} \right)$, k must have units of $\text{L}^{1/2}/\text{mol}^{1/2}\text{s}$.

26. a. $\text{Rate} = k[\text{I}]^x[\text{S}_2\text{O}_8^{2-}]^y$; $\frac{1.25 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.040)^x(0.040)^y}$, $2.00 = 2.0^x$, $x = 1$

$$\frac{1.25 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)(0.040)^y}{k(0.080)(0.020)^y}, 2.00 = 2.0^y, y = 1; \text{Rate} = k[\text{I}][\text{S}_2\text{O}_8^{2-}]$$

- b. For the first experiment:

$$\frac{12.5 \times 10^{-6} \text{ mol}}{\text{L s}} = k \left(\frac{0.080 \text{ mol}}{\text{L}} \right) \left(\frac{0.040 \text{ mol}}{\text{L}} \right), k = 3.9 \times 10^{-3} \text{ L/molXs}$$

Each of the other experiments also gives $k = 3.9 \times 10^{-3} \text{ L/molXs}$,

so $k_{\text{mean}} = 3.9 \times 10^{-3} \text{ L/molXs}$.

34. a. Because the $1/[\text{A}]$ vs. time plot was linear, the reaction is second order in A. The slope of the $1/[\text{A}]$ vs. time plot equals the rate constant k . Therefore, the rate law, the integrated rate law and the rate constant value are:

$$\text{Rate} = k[\text{A}]^2; \frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}; k = 3.60 \times 10^{-2} \text{ L/molXs}$$

- b. The half-life expression for a second-order reaction is: $t_{1/2} = \frac{1}{k[\text{A}]_0}$

$$\text{For this reaction: } t_{1/2} = \frac{1}{3.60 \times 10^{-2} \text{ L/mol} \cdot \text{s} \times 2.80 \times 10^{-3} \text{ mol/L}} = 9.92 \times 10^3 \text{ s}$$

Note: We could have used the integrated rate law to solve for $t_{1/2}$ where

$$[\text{A}] = (2.80 \times 10^{-3}/2) \text{ mol/L}.$$

- c. Since the half-life for a second-order reaction depends on concentration, we will use the integrated rate law to solve.

$$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}, \frac{1}{7.00 \times 10^{-4} \text{ M}} = \frac{3.60 \times 10^{-2} \text{ L}}{\text{mol} \cdot \text{s}} \times t + \frac{1}{2.80 \times 10^{-3} \text{ M}}$$

$$1.43 \times 10^3 + 357 = 3.60 \times 10^{-2} t, t = 2.98 \times 10^4 \text{ s}$$

40. The slope of the $1/[\text{A}]$ vs time plot in Exercise 12.39 with equal k .

$$\text{slope} = k = \frac{(60 - 20) \text{ L/mol}}{(5 - 1) \text{ s}} = 10 \text{ L/molXs}$$

a. $\frac{1}{[A]} = kt + \frac{1}{[A]_0} = \frac{10 \text{ L}}{\text{mol s}} \times 9 \text{ s} + \frac{1}{0.1 \text{ M}} = 100, [A] = 0.01 \text{ M}$

b. For a second-order reaction, the half-life does depend on concentration: $t_{1/2} = \frac{1}{k[A]_0}$

First half-life: $t_{1/2} = \frac{1}{\frac{10 \text{ L}}{\text{mol s}} \times \frac{0.1 \text{ mol}}{\text{L}}} = 1 \text{ s}$

Second half-life ($[A]_0$ is now 0.05 M): $t_{1/2} = 1/(10 \times 0.05) = 2 \text{ s}$

Third half-life ($[A]_0$ is now 0.025 M): $t_{1/2} = 1/(10 \times 0.025) = 4 \text{ s}$

47. Successive half-lives double as concentration is decreased by one-half. This is consistent with second-order reactions so assume the reaction is second order in A.

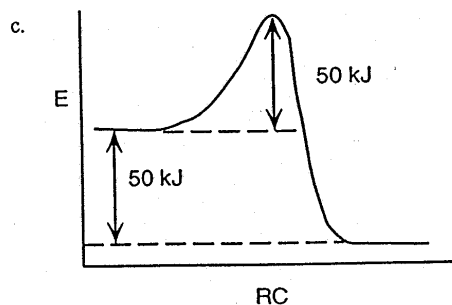
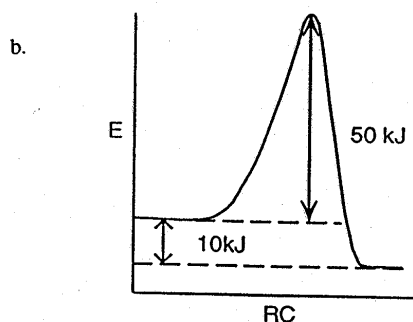
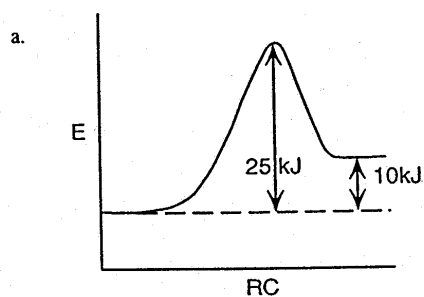
$$t_{1/2} = \frac{1}{k[A]_0}, k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{10.0 \text{ min}(0.10 \text{ M})} = 1.0 \text{ L/molXmin}$$

a. $\frac{1}{[A]} = kt + \frac{1}{[A]_0} = \frac{1.0 \text{ L}}{\text{mol min}} \times 80.0 \text{ min} + \frac{1}{0.10 \text{ M}} = 90. \text{ M}^{-1}, [A] = 1.1 \times 10^{-2} \text{ M}$

- b. $30.0 \text{ min} = 2 \text{ half-lives}$, so 25% of original A is remaining.

$$[A] = 0.25(0.10 \text{ M}) = 0.025 \text{ M}$$

54. When ΔE is positive, the products are at a higher energy relative to reactants and, when ΔE is negative, the products are at a lower energy relative to reactants.



60. For two conditions: $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ (Assuming A factor is T independent.)

$$\ln\left(\frac{8.1 \times 10^{-2} \text{ s}^{-1}}{4.6 \times 10^{-2} \text{ s}^{-1}}\right) = \frac{E_a}{8.3145 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{273 \text{ K}} - \frac{1}{293 \text{ K}} \right)$$

$$0.57 = \frac{E_a}{83145} (2.5 \times 10^{-4}), \quad E_a = 1.9 \times 10^4 \text{ J/mol} = 19 \text{ kJ/mol}$$

70. $\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k[A]^x$

Assuming the catalyzed and uncatalyzed reaction have the same form and orders and because concentrations are assumed equal, $\text{rate} \propto \frac{1}{\Delta t}$.

$$\frac{\text{rate}_{\text{cat}}}{\text{rate}_{\text{un}}} = \frac{\Delta t_{\text{un}}}{\Delta t_{\text{cat}}} = \frac{2400 \text{ yr}}{\Delta t_{\text{cat}}} \quad \text{and} \quad \frac{\text{rate}_{\text{cat}}}{\text{rate}_{\text{un}}} = \frac{k_{\text{cat}}}{k_{\text{un}}}$$

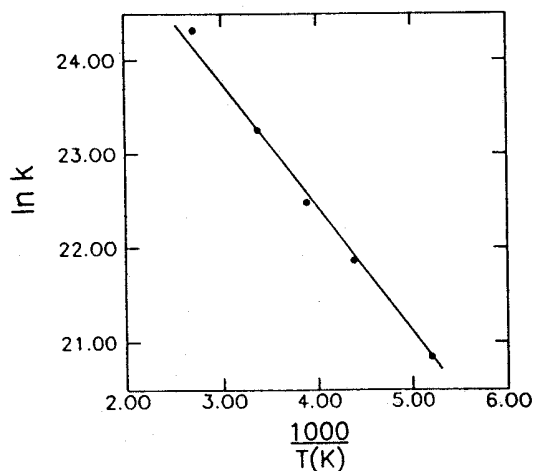
$$\frac{\text{rate}_{\text{cat}}}{\text{rate}_{\text{un}}} = \frac{k_{\text{cat}}}{k_{\text{un}}} = \frac{A \exp[-E_a(\text{cat})/RT]}{A \exp[-E_a(\text{un})/RT]} = \frac{\exp[-E_a(\text{cat}) + E_a(\text{un})]}{RT}$$

$$\frac{k_{\text{cat}}}{k_{\text{un}}} = \exp\left(\frac{-5.90 \times 10^4 \text{ J/mol} + 1.84 \times 10^5 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K} \times 600. \text{ K}}\right) = 7.62 \times 10^{10}$$

$$\frac{\Delta t_{\text{un}}}{\Delta t_{\text{cat}}} = \frac{\text{rate}_{\text{cat}}}{\text{rate}_{\text{un}}} = \frac{k_{\text{cat}}}{k_{\text{un}}}, \quad \frac{2400 \text{ yr}}{\Delta t_{\text{cat}}} = 7.62 \times 10^{10}, \quad \Delta t_{\text{cat}} = 3.15 \times 10^{-8} \text{ yr} \approx 1 \text{ sec}$$

74. The Arrhenius equation is: $k = A \exp(-E_a/RT)$ or in logarithmic form, $\ln k = -E_a/RT + \ln A$. Hence, a graph of $\ln k$ vs. $1/T$ should yield a straight line with a slope equal to $-E_a/R$ since the logarithmic form of the Arrhenius equation is in the form of a straight line equation, $y = mx + b$. Note: We carried one extra significant figure in the following $\ln k$ values in order to reduce round off error.

T (K)	1/T (K ⁻¹)	k (L/molXs)	ln k
195	5.13×10^{-3}	1.08×10^9	20.80
230.	4.35×10^{-3}	2.95×10^9	21.81
260.	3.85×10^{-3}	5.42×10^9	22.41
298	3.36×10^{-3}	12.0×10^9	23.21
369	2.71×10^{-3}	35.5×10^9	24.29



From "eyeballing" the line on the graph:

$$\text{slope} = \frac{20.95 - 23.65}{(5.00 \times 10^{-3} - 3.00 \times 10^{-3}) \text{ K}^{-1}} = \frac{-2.70}{2.00 \times 10^{-3}} = -1.35 \times 10^3 \text{ K} = \frac{-E_a}{R}$$

$$E_a = 1.35 \times 10^3 \text{ K} \times \frac{8.3145 \text{ J}}{\text{K mol}} = 1.12 \times 10^4 \text{ J/mol} = 11.2 \text{ kJ/mol}$$

From a graphing calculator: slope = $-1.43 \times 10^3 \text{ K}$ and $E_a = 11.9 \text{ kJ/mol}$

80. For second order kinetics: $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$ and $t_{1/2} = \frac{1}{k[A]_0}$

a. $\frac{1}{[A]} = (0.250 \text{ L/molXs})t + \frac{1}{[A]_0}$, $\frac{1}{[A]} = 0.250 \times 180. \text{ s} + \frac{1}{1.00 \times 10^{-2} \text{ M}}$

$$\frac{1}{[A]} = 145 \text{ M}^{-1}, [A] = 6.90 \times 10^{-3} \text{ M}$$

$$\text{Amount of A that reacted} = 0.0100 - 0.00690 = 0.0031 \text{ M}$$

$$[A_2] = \frac{1}{2} (3.1 \times 10^{-3} \text{ M}) = 1.6 \times 10^{-3} \text{ M}$$

b. After 3.00 minutes (180. s): $[A] = 3.00 [B]$, $6.90 \times 10^{-3} \text{ M} = 3.00 [B]$

$$[B] = 2.30 \times 10^{-3} \text{ M}$$

$$\frac{1}{[B]} = k_2 t + \frac{1}{[B]_0}, \frac{1}{2.30 \times 10^{-3} \text{ M}} = k_2 (180. \text{ s}) + \frac{1}{2.50 \times 10^{-2} \text{ M}}, k_2 = 2.19 \text{ L/molXs}$$

c. $t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{0.250 \text{ L/mol} \bullet \text{s} \times 1.00 \times 10^{-2} \text{ mol/L}} = 4.00 \times 10^2 \text{ s}$

91. $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right); \ln\left(\frac{1.7 \times 10^{-2} \text{ s}^{-1}}{7.2 \times 10^{-4} \text{ s}^{-1}}\right) = \frac{E_a}{8.3145 \text{ J/K} \bullet \text{mol}} \left(\frac{1}{660. \text{ K}} - \frac{1}{720. \text{ K}}\right)$

$$E_a = 2.1 \times 10^5 \text{ J/mol}$$

For k at 325°C (598 K):

$$\ln\left(\frac{1.7 \times 10^{-2} \text{ s}^{-1}}{k}\right) = \frac{2.1 \times 10^5 \text{ J/mol}}{8.3145 \text{ J/K} \bullet \text{mol}} \left(\frac{1}{598 \text{ K}} - \frac{1}{720. \text{ K}}\right), k = 1.3 \times 10^{-5} \text{ s}^{-1}$$

For three half-lives, we go from 100% \rightarrow 50% \rightarrow 25% \rightarrow 12.5%. After three half-lives, 12.5% of the original amount of $\text{C}_2\text{H}_5\text{I}$ remains. Partial pressures are directly related to gas concentrations in mol/L:

$$P_{\text{C}_2\text{H}_5\text{I}} = 894 \text{ torr} \times 0.125 = 112 \text{ torr after 3 half-lives}$$