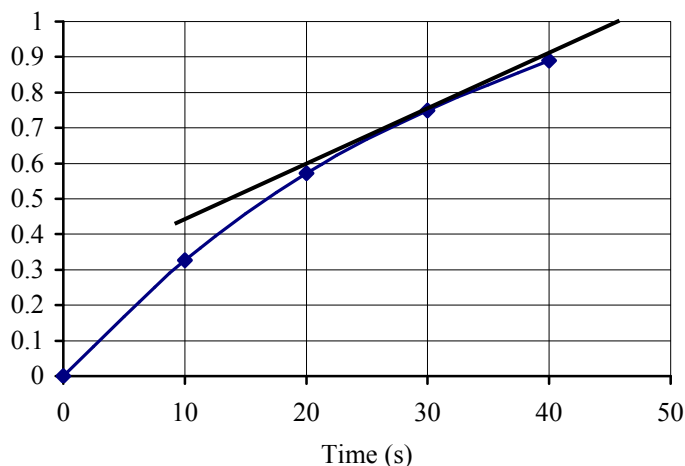


AP Chemistry – Chemical Kinetics (Kotz)

Homework Answers 5, 9, 11, 15, 19, 25, 29, 31, 33, 37, 43, 47, 51, 53, 73

15.5 (a)



$$\begin{aligned} \frac{\Delta[B]}{\Delta t} &= \frac{(0.326 - 0.000) \text{ mol/L}}{(10.0 - 0.00) \text{ s}} = 0.0326 \text{ mol/L} \cdot \text{s} \\ &= \frac{(0.572 - 0.326) \text{ mol/L}}{(20.0 - 10.0) \text{ s}} = 0.0246 \text{ mol/L} \cdot \text{s} \\ &= \frac{(0.750 - 0.572) \text{ mol/L}}{(30.0 - 20.0) \text{ s}} = 0.0178 \text{ mol/L} \cdot \text{s} \\ &= \frac{(0.890 - 0.750) \text{ mol/L}}{(40.0 - 30.0) \text{ s}} = 0.0140 \text{ mol/L} \cdot \text{s} \end{aligned}$$

The rate of change decreases from one time interval to the next due to the decrease in the amount of A remaining.

(b) A is consumed at half the rate B is formed. $\frac{\Delta[A]}{\Delta t} = -(0.0246 \text{ mol/L} \cdot \text{s})(1/2) = -0.0123 \text{ mol/L} \cdot \text{s}$

(c) Instantaneous rate is determined by drawing a tangent line to the plot at $[B] = 0.750 \text{ mol/L}$. The slope of this line is approximately $0.016 \text{ mol/L} \cdot \text{s}$

15.9 (a) Rate = $k[\text{NO}_2][\text{O}_3]$

(b) If the concentration of NO_2 is tripled, the rate will triple.

(c) If the concentration of O_3 is halved, the rate is halved.

15.11 (a) In the first two sets of data, $[\text{O}_2]$ is constant while $[\text{NO}]$ is doubled. The rate increases by a factor of four on going from the first set of data to the second, so the reaction is second order in NO . Looking at the first and third data sets, $[\text{NO}]$ is constant and $[\text{O}_2]$ doubles. The rate also doubles from the first data set to the third, so the reaction is first order in O_2 .

(b) Rate = $k[\text{NO}]^2[\text{O}_2]$

(c) Rate = $\frac{1}{2} \left(\frac{\Delta[\text{NO}]}{\Delta t} \right) = \frac{1}{2} (2.5 \times 10^{-5} \text{ mol/L} \cdot \text{s}) = 1.3 \times 10^{-5} \text{ mol/L} \cdot \text{s}$

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{1.3 \times 10^{-5} \text{ mol/L} \cdot \text{s}}{(0.010 \text{ mol/L})^2 (0.010 \text{ mol/L})} = 13 \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

$$(d) \text{ Rate} = k[\text{NO}]^2[\text{O}_2] = (13 \text{ L}^2/\text{mol}^2\cdot\text{s})(0.015 \text{ mol/L})^2(0.0050 \text{ mol/L}) = 1.4 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

$$(e) \text{ Rate at which O}_2 \text{ is reacting} = \frac{1.0 \times 10^{-4} \text{ mol/L}}{\text{s}} \cdot \frac{1 \text{ mol O}_2}{2 \text{ mol NO}} = 5.0 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

$$\text{Rate at which NO}_2 \text{ is forming} = \frac{1.0 \times 10^{-4} \text{ mol/L}}{\text{s}} \cdot \frac{2 \text{ mol NO}_2}{2 \text{ mol NO}} = 1.0 \times 10^{-4} \text{ mol/L}\cdot\text{s}$$

- 15.15 (a) Comparing experiment 1 to experiment 2, $[\text{O}_2]$ remains constant, $[\text{CO}]$ doubles, and the rate increases by a factor of four. The reaction is second order in CO. Comparing experiment 1 to experiment 3, $[\text{CO}]$ is constant, $[\text{O}_2]$ doubles, and the rate doubles. The reaction is first order in O_2 .

$$\text{Rate} = k[\text{CO}]^2[\text{O}_2]$$

- (b) The reaction is second order in CO, first order in O_2 , and third order overall.

$$(c) k = \frac{\text{Rate}}{[\text{CO}]^2[\text{O}_2]} = \frac{3.68 \times 10^{-5} \text{ mol/L}\cdot\text{min}}{(0.02 \text{ mol/L})^2(0.02 \text{ mol/L})} = 5 \text{ L}^2/\text{mol}^2\cdot\text{min}$$

$$15.19 \quad \ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -kt$$

$$\ln \left(\frac{0.31 \times 10^{-3} \text{ mol/L}}{1.24 \times 10^{-3} \text{ mol/L}} \right) = -(2.8 \times 10^{-3} \text{ min}^{-1})t$$

$$t = 5.0 \times 10^2 \text{ min}$$

- 15.25 The reaction is first order in N_2O_5

$$(a) t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.0 \times 10^{-4} \text{ s}^{-1}} = 1400 \text{ s}$$

$$(b) \ln \left(\frac{1}{10} \right) = -(5.0 \times 10^{-4} \text{ s}^{-1})t$$

$$t = 4600 \text{ s}$$

$$15.29 \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.70 \text{ h}} = 0.05457 \text{ h}^{-1}$$

$$\ln \frac{[{}^{64}\text{Cu}]}{[{}^{64}\text{Cu}]_0} = -(0.05457 \text{ h}^{-1})(64 \text{ h})$$

$$\text{fraction remaining} = \frac{[{}^{64}\text{Cu}]}{[{}^{64}\text{Cu}]_0} = 0.030$$

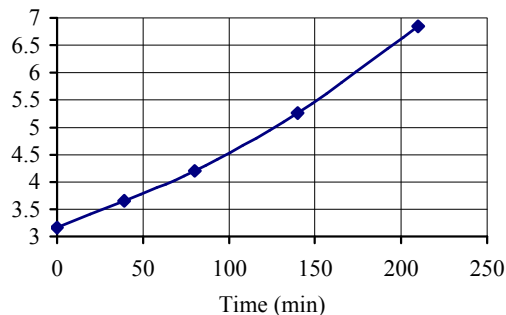
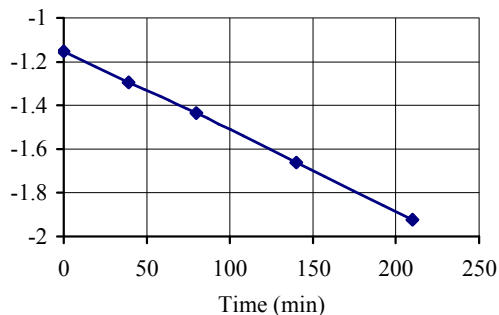
$$15.31 \quad \ln \left(\frac{25}{100} \right) = -k(72 \text{ s})$$

$$k = 0.019 \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.019 \text{ s}^{-1}} = 36 \text{ s}$$

Alternately, in a first-order reaction a sample decomposes 75% in two half-lives. $t_{1/2} = \frac{72 \text{ s}}{2} = 36 \text{ s}$

- 15.33 (a) The plot of $\ln[\text{sucrose}]$ versus time is linear so the reaction is first order in sucrose.



(b) $\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$

$$\ln\left(\frac{0.274 \text{ mol/L}}{0.316 \text{ mol/L}}\right) = -k(39 \text{ min})$$

$$k = 0.0037 \text{ min}^{-1}$$

(c) Using the $\ln[\text{sucrose}]$ versus time plot, $\ln[\text{sucrose}] = -1.79$ when $t = 175$

$$[\text{C}_{12}\text{H}_{22}\text{O}_{11}] = e^{-1.79} = 0.167 \text{ mol/L}$$

15.37 The reaction is second order in NO_2 $\text{Rate} = k[\text{NO}_2]^2$

$$k = \text{slope} = 1.1 \text{ L/mol}\cdot\text{s}$$

15.43 $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\ln\frac{k_2}{0.0315 \text{ s}^{-1}} = -\frac{260 \text{ kJ/mol}}{8.3145 \times 10^{-3} \text{ kJ/K}\cdot\text{mol}}\left(\frac{1}{850 \text{ K}} - \frac{1}{800 \text{ K}}\right)$$

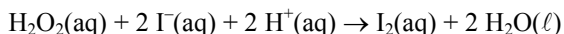
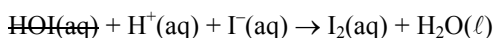
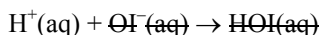
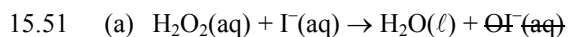
$$\ln(k_2) - \ln(0.0315 \text{ s}^{-1}) = -\frac{260 \text{ kJ/mol}}{8.3145 \times 10^{-3} \text{ kJ/K}\cdot\text{mol}}\left(\frac{1}{850 \text{ K}} - \frac{1}{800 \text{ K}}\right)$$

$$k_2 = 0.3 \text{ s}^{-1}$$

15.47 (a) $\text{Rate} = k[\text{NO}][\text{NO}_3]$

(b) $\text{Rate} = k[\text{Cl}][\text{H}_2]$

(c) $\text{Rate} = k[(\text{CH}_3)_3\text{CBr}]$

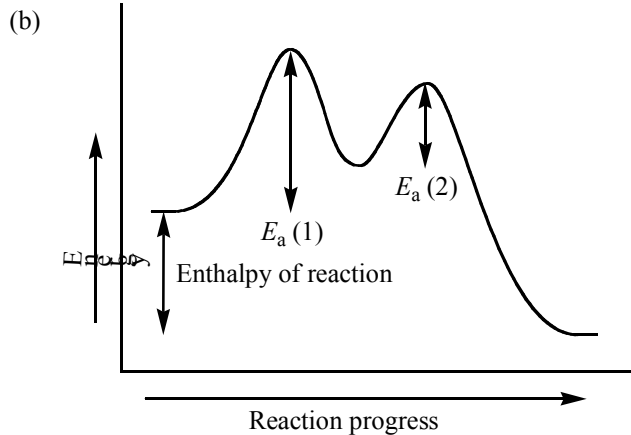


(b) Step 1 and Step 2 are bimolecular, Step 3 is termolecular.

(c) $\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$

(d) $\text{OI}^-(\text{aq})$ and $\text{HOI}(\text{aq})$ are intermediates.

15.53 (a) Reactants: $\text{NO}_2(\text{g}), \text{CO}(\text{g})$ Products: $\text{NO}(\text{g}), \text{CO}_2(\text{g})$ Intermediate: NO_3



15.73 (a) $2 \text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{BrNO}(\text{g})$

(b) Mechanism 1: termolecular

Mechanism 2: Step 1: bimolecular

Step 2: bimolecular

Mechanism 3: Step 1: bimolecular

Step 2: bimolecular

(c) Mechanism 2: $\text{Br}_2\text{NO}(\text{g})$ is an intermediate

Mechanism 3 $\text{N}_2\text{O}_2(\text{g})$ is an intermediate

(d) The rate equations will all differ. Mechanism 1 would be second order in NO and first order in Br_2 .

Mechanism 2 would be first order in both NO and Br_2 . Finally, Mechanism 3 would be second order in NO and zero order in Br_2 .