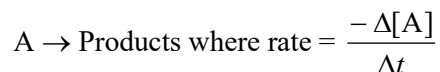


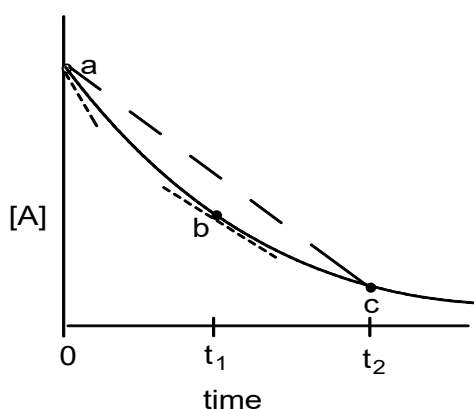
Chapter 11 Review Questions and Text Homework Solutions

Review Questions

1. The reaction rate is defined as the change in concentration of a reactant or product per unit time. Consider the general reaction:



If we graph $[A]$ vs. t , it will usually look like the solid line in the following plot.



An instantaneous rate is the slope of a tangent line to the graph of $[A]$ vs. t . We can determine the instantaneous rate at any time during the reaction. On the plot, tangent lines at $t \approx 0$ and $t = t_1$ are drawn. The slope of these tangent lines would be the instantaneous rates at $t \approx 0$ and $t = t_1$. We call the instantaneous rate at $t \approx 0$ the initial rate. The average rate is measured over a period of time. For example, the slope of the dashed line connecting points a and c is the average rate of the reaction over the entire length of time 0 to t_2 (average rate = $\Delta[A]/\Delta t$). An average rate is determined over some time period, whereas an instantaneous rate is determined at one specific time. The rate that is largest is generally the initial rate. At $t \approx 0$, the slope of the tangent line is greatest, which means the rate is largest at $t \approx 0$.

The initial rate is used by convention so that the rate of reaction only depends on the forward reaction; at $t \approx 0$, the reverse reaction is insignificant because no products are present yet.

2. The differential rate law describes the dependence of the rate on the concentration of reactants. The integrated rate law expresses reactant concentrations as a function of time. The differential rate law is generally just called the rate law. The rate constant k is a constant that allows one to equate the rate of a reaction to the concentration of reactants. The order is the exponent that the reactant concentrations are raised to in the rate equation.
3. The method of initial rates uses the results from several experiments where each experiment is carried out at a different set of initial reactant concentrations and the initial rate is determined. The

results of the experiments are compared to see how the initial rate depends on the initial concentrations. If possible, two experiments are compared where only one reactant concentration changes. For these two experiments, any change in the initial rate must be due to the change in that one reactant concentration. The results of the experiments are compared until all of the orders are determined. After the orders are determined, then one can go back to any (or all) of the experiments and set the initial rate equal to the rate law using the concentrations in that experiment. The only unknown is k , which is then solved for. The units on k depend on the orders in the rate law. Because there are many different rate laws, there are many different units for k .

Rate = $k[A]^n$; for a first-order rate law, $n = 1$. If $[A]$ is tripled, then the rate is tripled. When $[A]$ is quadrupled (increased by a factor of four), and the rate increases by a factor of 16, then A must be second order ($4^2 = 16$). For a third order reaction, as $[A]$ is doubled, the rate will increase by a factor of $2^3 = 8$. For a zero-order reaction, the rate is independent of the concentration of A. The only stipulation for zero order reactions is that the reactant or reactants must be present; if they are, then the rate is a constant value (rate = k).

5. The integrated rate laws can be put into the equation for a straight line, $y = mx + b$ where x and y are the x and y axes, m is the slope of the line, and b is the y -intercept.

Zero order:
$$\begin{array}{l} [A] = -kt + [A]_0 \\ y = mx + b \end{array}$$

A plot of $[A]$ vs. time will be linear with a negative slope equal to $-k$ and a y -intercept equal to $[A]_0$.

First order:
$$\begin{array}{l} \ln[A] = -kt + \ln[A]_0 \\ y = mx + b \end{array}$$

A plot of $\ln[A]$ vs. time will be linear with a negative slope equal to $-k$ and a y -intercept equal to $\ln[A]_0$.

Second order:
$$\begin{array}{l} \frac{1}{[A]} = kt + \frac{1}{[A]_0} \\ y = mx + b \end{array}$$

A plot of $1/[A]$ vs. time will be linear with a positive slope equal to k and a y -intercept equal to $1/[A]_0$.

When two or more reactants are studied, only one of the reactants is allowed to change during any one experiment. This is accomplished by having a large excess of the other reactant(s) as compared to the reactant studied; so large that the concentration of the other reactant(s) stays effectively constant during the experiment. The slope of the straight-line plot equals k (or $-k$) multiplied by the other reactant concentrations raised to the correct orders. Once all the orders are known for a reaction, then any (or all) of the slopes can be used to determine k .

6. At $t = t_{1/2}$, $[A] = 1/2[A]_0$; plugging these terms into the integrated rate laws yields the following half-life expressions:

zero order

$$t_{1/2} = \frac{[A]_0}{2k}$$

first order

$$t_{1/2} = \frac{\ln 2}{k}$$

second order

$$t_{1/2} = \frac{1}{k[A]_0}$$

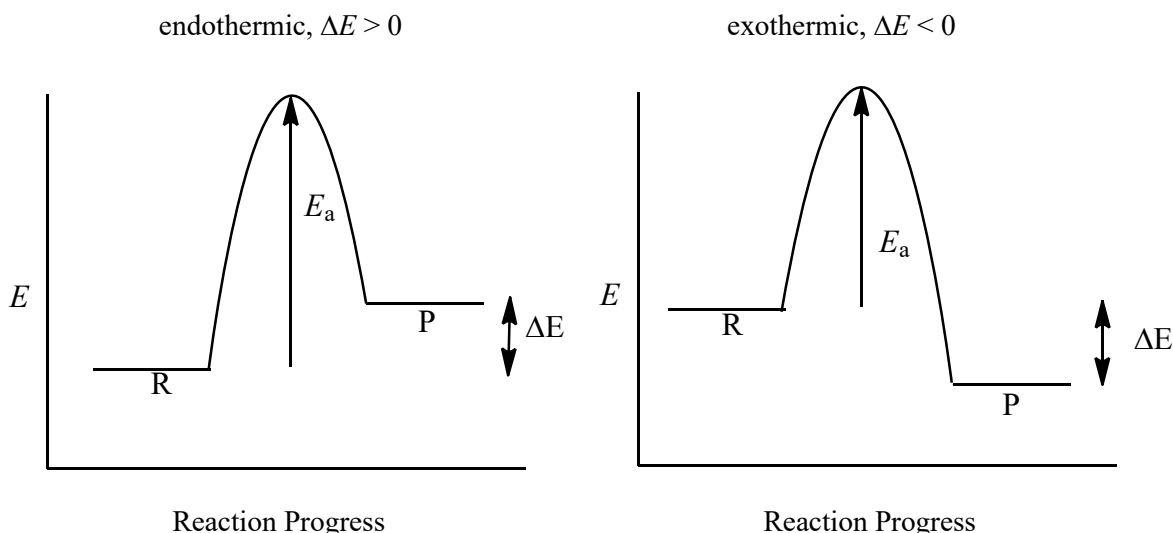
The first order half-life is independent of concentration, the zero order half-life is directly related to the concentration, and the second order half-life is inversely related to concentration. For a first order reaction, if the first half-life equals 20. s, the second half-life will also be 20. s because the half-life for a first order reaction is concentration independent. The second half-life for a zero-order reaction will be $1/2(20.) = 10.$ s. This is because the half-life for a zero-order reaction has a direct relationship with concentration (as the concentration decreases by a factor of 2, the half-life decreases by a factor of 2). For a second order reaction which has an inverse relationship between $t_{1/2}$ and $[A]_0$, the second half-life will be 40. s (twice the first half-life value).

7.
 - a. An elementary step (reaction) is one for which the rate law can be written from the molecularity, i.e., from coefficients in the balanced equation.
 - b. The molecularity is the number of species that must collide to produce the reaction represented by an elementary step in a reaction mechanism.
 - c. The mechanism of a reaction is the series of proposed elementary reactions that may occur to give the overall reaction. The sum of all the steps in the mechanism gives the balanced chemical reaction.
 - d. An intermediate is a species that is neither a reactant nor a product but that is formed and consumed in the reaction sequence.
 - e. The rate-determining step is the slowest elementary reaction in any given mechanism.
8. For a mechanism to be acceptable, the sum of the elementary steps must give the overall balanced equation for the reaction, and the mechanism must give a rate law that agrees with the experimentally determined rate law. A mechanism can never be proven absolutely. We can only say it is possibly correct if it follows the two requirements described above.

Most reactions occur by a series of steps. If most reactions were unimolecular, then most reactions would have a first order overall rate law, which is not the case.

9. The premise of the collision model is that molecules must collide to react, but not all collisions between reactant molecules result in product formation.
 - a. The larger the activation energy, the slower the rate.
 - b. The higher the temperature, the more molecular collisions with sufficient energy to convert to products and the faster the rate.
 - c. The greater the frequency of collisions, the greater the opportunities for molecules to react, and, hence, the greater the rate.

- d. For a reaction to occur, it is the reactive portion of each molecule that must be involved in a collision. Only some of all the possible collisions have the correct orientation to convert reactants to products.



The activation energy for the reverse reaction will be the energy difference between the products and the transition state at the top of the potential energy “hill.” For an exothermic reaction, the activation energy for the reverse reaction ($E_{a,r}$) is larger than the activation energy for the forward reaction (E_a), so the rate of the forward reaction will be greater than the rate of the reverse reaction. For an endothermic reaction, $E_{a,r} < E_a$ so the rate of the forward reaction will be less than the rate of the reverse reaction (with other factors being equal).

11. A catalyst increases the rate of a reaction by providing reactants with an alternate pathway (mechanism) to convert to products. This alternate pathway has a lower activation energy, thus increasing the rate of the reaction.

A homogeneous catalyst is one that is in the same phase as the reacting molecules, and a heterogeneous catalyst is in a different phase than the reactants. The heterogeneous catalyst is usually a solid, although a catalyst in a liquid phase can act as a heterogeneous catalyst for some gas phase reactions. Since the catalyzed reaction has a different mechanism than the uncatalyzed reaction, the catalyzed reaction most likely will have a different rate law.

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13. All these choices would affect the rate of the reaction, but only b and c affect the rate by affecting the value of the rate constant k . The value of the rate constant depends on temperature. The value of the rate constant also depends on the activation energy. A catalyst will change the value of k because the activation energy changes. Increasing the concentration (partial pressure) of either O_2 or NO does not affect the value of k , but it does increase the rate of the reaction because both concentrations appear in the rate law.

$$17. \quad \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]_2^x}{k[A]_1^x} = \left(\frac{[A]_2}{[A]_1} \right)^x$$

The rate doubles as the concentration quadruples:

$$2 = (4)^x, \quad x = 1/2$$

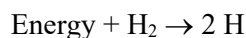
The order is 1/2 (the square root of the concentration of reactant).

For a reactant that has an order of -1 and the reactant concentration is doubled:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = (2)^{-1} = \frac{1}{2}$$

The rate will decrease by a factor of 1/2 when the reactant concentration is doubled for a -1 order reaction. Negative orders are seen for substances that hinder or slow down a reaction.

18. Some energy must be added to get the reaction started, that is, to overcome the activation energy barrier. Chemically what happens is:



The hydrogen atoms initiate a chain reaction that proceeds very rapidly. Collisions of H_2 and O_2 molecules at room temperature do not have sufficient kinetic energy to form hydrogen atoms and initiate the reaction.

19. Two reasons are:

- (1) The collision must involve enough energy to produce the reaction; that is, the collision energy must be equal to or exceed the activation energy.
- (2) The relative orientation of the reactants when they collide must allow formation of any new bonds necessary to produce products.

20. a. The blue plot is the catalyzed pathway. The catalyzed pathway has the lower activation. Therefore, the catalyzed pathway is faster.
- b. ΔE_1 represents the activation energy for the uncatalyzed pathway.
- c. ΔE_2 represents the energy difference between the reactants and products. Note that ΔE_2 is the same for both the catalyzed and the uncatalyzed pathways. It is the activation energy that is different for a catalyzed pathway versus an uncatalyzed pathway.
- d. Because the products have a higher total energy as compared to reactants, this is an endothermic reaction.

23. The coefficients in the balanced reaction relate the rate of disappearance of reactants to the rate of production of products. From the balanced reaction, the rate of production of P_4 will be 1/4 the

rate of disappearance of PH_3 , and the rate of production of H_2 will be 6/4 the rate of disappearance of PH_3 . By convention, all rates are given as positive values.

$$\text{Rate} = \frac{-\Delta[\text{PH}_3]}{\Delta t} = \frac{-(-0.048 \text{ mol}/2.0 \text{ L})}{\text{s}} = 2.4 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

$$\frac{\Delta[\text{P}_4]}{\Delta t} = -\frac{1}{4} \frac{\Delta[\text{PH}_3]}{\Delta t} = 2.4 \times 10^{-3} / 4 = 6.0 \times 10^{-4} \text{ mol/L}\cdot\text{s}$$

$$\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{6}{4} \frac{\Delta[\text{PH}_3]}{\Delta t} = 6(2.4 \times 10^{-3})/4 = 3.6 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

26. $0.0120/0.0080 = 1.5$; reactant B is used up 1.5 times faster than reactant A. This corresponds to a 3 to 2 mole 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 $2\text{A} + 3\text{B} \rightarrow 4\text{C}$.

29. a. In the first two experiments, $[\text{NO}]$ is held constant and $[\text{Cl}_2]$ is doubled. The rate also doubled. Thus the reaction is first order with respect to Cl_2 . Or mathematically, $\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$.

$$\frac{0.36}{0.18} = \frac{k(0.10)^x(0.20)^y}{k(0.10)^x(0.10)^y} = \frac{(0.20)^y}{(0.10)^y}, \quad 2.0 = 2.0^y, \quad y = 1$$

We can get the dependence on NO from the second and third experiments. Here, as the NO concentration doubles (Cl_2 concentration is constant), the rate increases by a factor of four. Thus the reaction is second order with respect to NO. Or mathematically:

$$\frac{1.45}{0.36} = \frac{k(0.20)^x(0.20)}{k(0.10)^x(0.20)} = \frac{(0.20)^x}{(0.10)^x}, \quad 4.0 = 2.0^x, \quad x = 2; \quad \text{so Rate} = k[\text{NO}]^2[\text{Cl}_2].$$

Try to examine experiments where only one concentration changes at a time. The more variables that change, the harder it is to determine the orders. Also, these types of problems can usually be solved by inspection. In general, we will solve using a mathematical approach, but keep in mind that you probably can solve for the orders by simple inspection of the data.

- b. The rate constant k can be determined from the experiments. From experiment 1:

$$\frac{0.18 \text{ mol}}{\text{L min}} = k \left(\frac{0.10 \text{ mol}}{\text{L}} \right)^2 \left(\frac{0.10 \text{ mol}}{\text{L}} \right), \quad k = 180 \text{ L}^2/\text{mol}^2\cdot\text{min}$$

From the other experiments:

$$k = 180 \text{ L}^2/\text{mol}^2\cdot\text{min} \text{ (second exp.)}; \quad k = 180 \text{ L}^2/\text{mol}^2\cdot\text{min} \text{ (third exp.)}$$

The average rate constant is $k_{\text{mean}} = 1.8 \times 10^2 \text{ L}^2/\text{mol}^2\cdot\text{min}$.

31. a. $\text{Rate} = k[\text{NOCl}]^n$; using experiments two and three:

$$\frac{2.66 \times 10^4}{6.64 \times 10^3} = \frac{k(2.0 \times 10^{16})^n}{k(1.0 \times 10^{16})^n}, \quad 4.01 = 2.0^n, \quad n = 2; \quad \text{Rate} = k[\text{NOCl}]^2$$

$$\text{b. } \frac{5.98 \times 10^4 \text{ molecules}}{\text{cm}^3 \text{ s}} = k \left(\frac{3.0 \times 10^{16} \text{ molecules}}{\text{cm}^3} \right)^2, \quad k = 6.6 \times 10^{-29} \text{ cm}^3/\text{molecules}\cdot\text{s}$$

The other three experiments give $(6.7, 6.6, \text{ and } 6.6) \times 10^{-29} \text{ cm}^3/\text{molecules}\cdot\text{s}$, respectively. The mean value for k is $6.6 \times 10^{-29} \text{ cm}^3/\text{molecules}\cdot\text{s}$.

$$\text{c. } \frac{6.6 \times 10^{-29} \text{ cm}^3}{\text{molecules s}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = \frac{4.0 \times 10^{-8} \text{ L}}{\text{mol s}}$$

34. Rate = $k[\text{NO}]^x[\text{O}_2]^y$; comparing the first two experiments, $[\text{O}_2]$ is unchanged, $[\text{NO}]$ is tripled, and the rate increases by a factor of nine. Therefore, the reaction is second order in NO ($3^2 = 9$). The order of O_2 is more difficult to determine. Comparing the second and third experiments:

$$\frac{3.13 \times 10^{17}}{1.80 \times 10^{17}} = \frac{k(2.50 \times 10^{18})^2(2.50 \times 10^{18})^y}{k(3.00 \times 10^{18})^2(1.00 \times 10^{18})^y}$$

$$1.74 = 0.694(2.50)^y, \quad 2.51 = 2.50^y, \quad y = 1$$

Rate = $k[\text{NO}]^2[\text{O}_2]$; from experiment 1:

$$2.00 \times 10^{16} \text{ molecules/cm}^3\cdot\text{s} = k(1.00 \times 10^{18} \text{ molecules/cm}^3)^2 \times (1.00 \times 10^{18} \text{ molecules/cm}^3)$$

$$k = 2.00 \times 10^{-38} \text{ cm}^6/\text{molecules}^2\cdot\text{s} = k_{\text{mean}}$$

$$\text{Rate} = \frac{2.00 \times 10^{-38} \text{ cm}^6}{\text{molecules}^2 \text{ s}} \times \left(\frac{6.21 \times 10^{18} \text{ molecules}}{\text{cm}^3} \right)^2 \times \frac{7.36 \times 10^{18} \text{ molecules}}{\text{cm}^3}$$

$$\text{Rate} = 5.68 \times 10^{18} \text{ molecules/cm}^3\cdot\text{s}$$

36. a. Rate = $k[\text{ClO}_2]^x[\text{OH}^-]^y$; from the first two experiments:

$$2.30 \times 10^{-1} = k(0.100)^x(0.100)^y \quad \text{and} \quad 5.75 \times 10^{-2} = k(0.0500)^x(0.100)^y$$

$$\text{Dividing the two rate laws: } 4.00 = \frac{(0.100)^x}{(0.0500)^x} = 2.00^x, \quad x = 2$$

Comparing the second and third experiments:

$$2.30 \times 10^{-1} = k(0.100)(0.100)^y \quad \text{and} \quad 1.15 \times 10^{-1} = k(0.100)(0.0500)^y$$

$$\text{Dividing: } 2.00 = \frac{(0.100)^y}{(0.050)^y} = 2.0^y, \quad y = 1$$

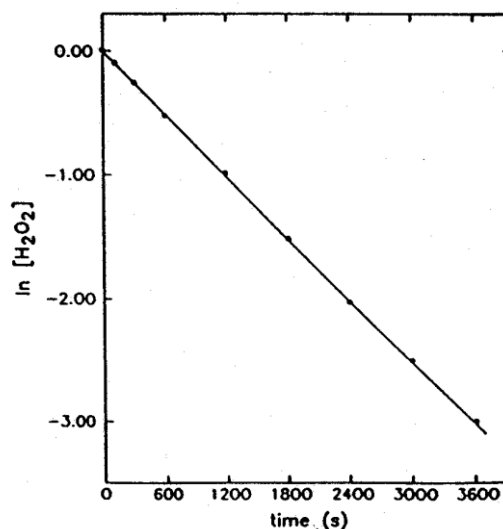
The rate law is Rate = $k[\text{ClO}_2]^2[\text{OH}^-]$.

$$2.30 \times 10^{-1} \text{ mol/L}\cdot\text{s} = k(0.100 \text{ mol/L})^2(0.100 \text{ mol/L}), \quad k = 2.30 \times 10^2 \text{ L}^2/\text{mol}^2\cdot\text{s} = k_{\text{mean}}$$

$$\text{b. Rate} = \frac{2.30 \times 10^2 \text{ L}^2}{\text{mol}^2 \text{ s}} \times \left(\frac{0.175 \text{ mol}}{\text{L}} \right)^2 \times \frac{0.0844 \text{ mol}}{\text{L}} = 0.594 \text{ mol/L}\cdot\text{s}$$

37. The first assumption to make is that the reaction is first order. For a first order reaction, a graph of $\ln[\text{H}_2\text{O}_2]$ versus time will yield a straight line. If this plot is not linear, then the reaction is not first order, and we make another assumption.

Time (s)	$[\text{H}_2\text{O}_2]$ (mol/L)	$\ln[\text{H}_2\text{O}_2]$
0	1.00	0.000
120.	0.91	-0.094
300.	0.78	-0.25
600.	0.59	-0.53
1200.	0.37	-0.99
1800.	0.22	-1.51
2400.	0.13	-2.04
3000.	0.082	-2.50
3600.	0.050	-3.00



Note: We carried extra significant figures in some of the natural log values in order to reduce round-off error. For the plots, we will do this most of the time when the natural log function is involved.

The plot of $\ln[\text{H}_2\text{O}_2]$ versus time is linear. Thus the reaction is first order. The rate law and integrated rate law are $\text{Rate} = k[\text{H}_2\text{O}_2]$ and $\ln[\text{H}_2\text{O}_2] = -kt + \ln[\text{H}_2\text{O}_2]_0$.

We determine the rate constant k by determining the slope of the $\ln[\text{H}_2\text{O}_2]$ versus time plot (slope = $-k$). Using two points on the curve gives:

$$\text{slope} = -k = \frac{\Delta y}{\Delta x} = \frac{0 - (3.00)}{0 - 3600} = -8.3 \times 10^{-4} \text{ s}^{-1}, \quad k = 8.3 \times 10^{-4} \text{ s}^{-1}$$

To determine $[\text{H}_2\text{O}_2]$ at 4000. s, use the integrated rate law, where $[\text{H}_2\text{O}_2]_0 = 1.00 \text{ M}$.

$$\ln[\text{H}_2\text{O}_2] = -kt + \ln[\text{H}_2\text{O}_2]_0 \quad \text{or} \quad \ln\left(\frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0}\right) = -kt$$

$$\ln\left(\frac{[\text{H}_2\text{O}_2]}{1.00}\right) = -8.3 \times 10^{-4} \text{ s}^{-1} \times 4000. \text{ s}, \quad \ln[\text{H}_2\text{O}_2] = -3.3, \quad [\text{H}_2\text{O}_2] = e^{-3.3} = 0.037 \text{ M}$$

38. a. Because the $\ln[A]$ versus time plot was linear, the reaction is first order in A. The slope of the $\ln[A]$ versus time plot equals $-k$. Therefore, the rate law, the integrated rate law, and the rate constant value are:

$$\text{Rate} = k[A]; \ln[A] = -kt + \ln[A]_0; k = 2.97 \times 10^{-2} \text{ min}^{-1}$$

- b. The half-life expression for a first order rate law is:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}, \quad t_{1/2} = \frac{0.6931}{2.97 \times 10^{-2} \text{ min}^{-1}} = 23.3 \text{ min}$$

- c. $2.50 \times 10^{-3} M$ is $1/8$ of the original amount of A present initially, so the reaction is 87.5% complete. When a first-order reaction is 87.5% complete (or 12.5% remains), then the reaction has gone through 3 half-lives:

$$100\% \xrightarrow{t_{1/2}} 50.0\% \xrightarrow{t_{1/2}} 25.0\% \xrightarrow{t_{1/2}} 12.5\%; \quad t = 3 \times t_{1/2} = 3 \times 23.3 \text{ min} = 69.9 \text{ min}$$

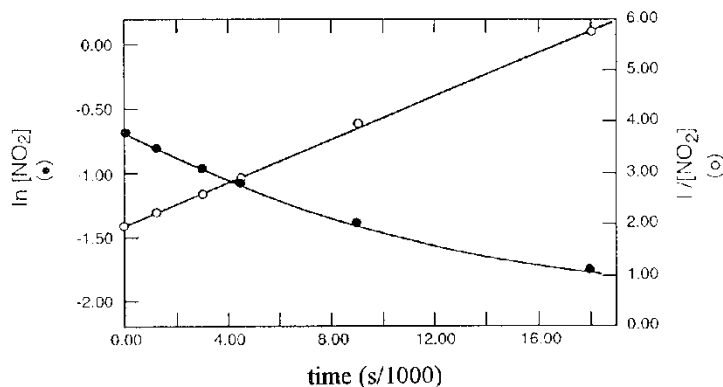
Or we can use the integrated rate law:

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt, \quad \ln\left(\frac{2.50 \times 10^{-3} M}{2.00 \times 10^{-2} M}\right) = -(2.97 \times 10^{-2} \text{ min}^{-1})t$$

$$t = \frac{\ln(0.125)}{-2.97 \times 10^{-2} \text{ min}^{-1}} = 70.0 \text{ min}$$

39. Assume the reaction is first order and see if the plot of $\ln[\text{NO}_2]$ versus time is linear. If this isn't linear, try the second-order plot of $1/[\text{NO}_2]$ versus time because second-order reactions are the next most common after first-order reactions. The data and plots follow.

Time (s)	$[\text{NO}_2] (M)$	$\ln[\text{NO}_2]$	$1/[\text{NO}_2] (M^{-1})$
0	0.500	-0.693	2.00
1.20×10^3	0.444	-0.812	2.25
3.00×10^3	0.381	-0.965	2.62
4.50×10^3	0.340	-1.079	2.94
9.00×10^3	0.250	-1.386	4.00
1.80×10^4	0.174	-1.749	5.75



The plot of $1/[\text{NO}_2]$ versus time is linear. The reaction is second order in NO_2 .

The rate law and integrated rate law are: $\text{Rate} = k[\text{NO}_2]^2$ and $\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$

The slope of the plot $1/[\text{NO}_2]$ vs. t gives the value of k . Using a couple of points on the plot:

$$\text{slope} = k = \frac{\Delta y}{\Delta x} = \frac{(5.75 - 2.00) \text{ M}^{-1}}{(1.80 \times 10^4 - 0) \text{ s}} = 2.08 \times 10^{-4} \text{ L/mol}\cdot\text{s}$$

To determine $[\text{NO}_2]$ at $2.70 \times 10^4 \text{ s}$, use the integrated rate law, where $1/[\text{NO}_2]_0 = 1/0.500 \text{ M} = 2.00 \text{ M}^{-1}$.

$$\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}, \quad \frac{1}{[\text{NO}_2]} = \frac{2.08 \times 10^{-4} \text{ L}}{\text{mol s}} \times 2.70 \times 10^4 \text{ s} + 2.00 \text{ M}^{-1}$$

$$\frac{1}{[\text{NO}_2]} = 7.62, \quad [\text{NO}_2] = 0.131 \text{ M}$$

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

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

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

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

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

41. a. Because the $[\text{C}_2\text{H}_5\text{OH}]$ versus time plot was linear, the reaction is zero order in $\text{C}_2\text{H}_5\text{OH}$. The slope of the $[\text{C}_2\text{H}_5\text{OH}]$ versus time plot equals $-k$. Therefore, the rate law, the integrated rate law, and the rate constant value are: $\text{Rate} = k[\text{C}_2\text{H}_5\text{OH}]^0 = k$; $[\text{C}_2\text{H}_5\text{OH}] = -kt + [\text{C}_2\text{H}_5\text{OH}]_0$; $k = 4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s}$
- b. The half-life expression for a zero-order reaction is $t_{1/2} = [\text{A}]_0/2k$.

$$t_{1/2} = \frac{[\text{C}_2\text{H}_5\text{OH}]_0}{2k} = \frac{1.25 \times 10^{-2} \text{ mol/L}}{2 \times 4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s}} = 156 \text{ s}$$

Note: We could have used the integrated rate law to solve for $t_{1/2}$, where $[\text{C}_2\text{H}_5\text{OH}] = (1.25 \times 10^{-2}/2) \text{ mol/L}$.

c. $[\text{C}_2\text{H}_5\text{OH}] = -kt + [\text{C}_2\text{H}_5\text{OH}]_0$, $0 \text{ mol/L} = -(4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s})t + 1.25 \times 10^{-2} \text{ mol/L}$

$$t = \frac{1.25 \times 10^{-2} \text{ mol/L}}{4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s}} = 313 \text{ s}$$

45. Because the $1/[\text{A}]$ versus time plot is linear with a positive slope, the reaction is second order with respect to A. The y intercept in the plot will equal $1/[\text{A}]_0$. Extending the plot, the y intercept will be about 10, so $1/10 = 0.1 \text{ M} = [\text{A}]_0$.

46. a. The slope of the $1/[\text{A}]$ versus time plot in Exercise 45 will equal k.

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

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

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

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

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

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

47. a. $[\text{A}] = -kt + [\text{A}]_0$; if $k = 5.0 \times 10^{-2} \text{ mol/L}\cdot\text{s}$ and $[\text{A}]_0 = 1.00 \times 10^{-3} \text{ M}$, then:

$$[\text{A}] = -(5.0 \times 10^{-2} \text{ mol/L}\cdot\text{s})t + 1.00 \times 10^{-3} \text{ mol/L}$$

- b. $\frac{[\text{A}]_0}{2} = -(5.0 \times 10^{-2})t_{1/2} + [\text{A}]_0$ because at $t = t_{1/2}$, $[\text{A}] = [\text{A}]_0/2$.

$$-0.50[\text{A}]_0 = -(5.0 \times 10^{-2})t_{1/2}, t_{1/2} = \frac{0.50(1.00 \times 10^{-3})}{5.0 \times 10^{-2}} = 1.0 \times 10^{-2} \text{ s}$$

Note: We could have used the $t_{1/2}$ expression to solve ($t_{1/2} = \frac{[\text{A}]_0}{2k}$).

- c. $[\text{A}] = -kt + [\text{A}]_0 = -(5.0 \times 10^{-2} \text{ mol/L}\cdot\text{s})(5.0 \times 10^{-3} \text{ s}) + 1.00 \times 10^{-3} \text{ mol/L}$

$$[\text{A}] = 7.5 \times 10^{-4} \text{ mol/L}$$

$$[\text{A}]_{\text{reacted}} = 1.00 \times 10^{-3} \text{ mol/L} - 7.5 \times 10^{-4} \text{ mol/L} = 2.5 \times 10^{-4} \text{ mol/L}$$

$$[\text{B}]_{\text{produced}} = [\text{A}]_{\text{reacted}} = 2.5 \times 10^{-4} \text{ M}$$

51. For a first-order reaction, the integrated rate law is $\ln([A]/[A]_0) = -kt$. Solving for k :

$$\ln\left(\frac{0.250 \text{ mol/L}}{1.00 \text{ mol/L}}\right) = -k \times 120. \text{ s}, \quad k = 0.0116 \text{ s}^{-1}$$

$$\ln\left(\frac{0.350 \text{ mol/L}}{2.00 \text{ mol/L}}\right) = -0.0116 \text{ s}^{-1} \times t, \quad t = 150. \text{ S}$$

53. Comparing experiments 1 and 2, as the concentration of AB is doubled, the initial rate increases by a factor of 4. The reaction is second order in AB.

$$\text{Rate} = k[\text{AB}]^2, \quad 3.20 \times 10^{-3} \text{ mol/L}\cdot\text{s} = k(0.200 \text{ M})^2$$

$$k = 8.00 \times 10^{-2} \text{ mol/L}\cdot\text{s} = k_{\text{mean}}$$

For a second order reaction:

$$t_{1/2} = \frac{1}{k[\text{AB}]_0} = \frac{1}{8.00 \times 10^{-2} \text{ L/mol}\cdot\text{s} \times 1.00 \text{ mol/L}} = 12.5 \text{ s}$$

54. a. The integrated rate law for a second order reaction is $1/[A] = kt + 1/[A]_0$, and the half-life expression is $t_{1/2} = 1/k[A]_0$. We could use either to solve for $t_{1/2}$. Using the integrated rate law:

$$\frac{1}{(0.900/2) \text{ mol/L}} = k \times 2.00 \text{ s} + \frac{1}{0.900 \text{ mol/L}}, \quad k = \frac{1.11 \text{ L/mol}}{2.00 \text{ s}} = 0.555 \text{ L/mol}\cdot\text{s}$$

b. $\frac{1}{0.100 \text{ mol/L}} = 0.555 \text{ L/mol}\cdot\text{s} \times t + \frac{1}{0.900 \text{ mol/L}}, \quad t = \frac{8.9 \text{ L/mol}}{0.555 \text{ L/mol}\cdot\text{s}} = 16 \text{ s}$

55. 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.

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

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

- b. 30.0 min = 2 half-lives, so 25% of original A is remaining.

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

57. Because $[V]_0 \gg [AV]_0$, the concentration of V is essentially constant in this experiment. We have a pseudo-first-order reaction in AV:

$$\text{Rate} = k[AV][V] = k'[AV], \quad \text{where } k' = k[V]_0$$

The slope of the $\ln[A/V]$ versus time plot is equal to $-k'$.

$$k' = -\text{slope} = 0.32 \text{ s}^{-1}; \quad k = \frac{k'}{[V]_0} = \frac{0.32 \text{ s}^{-1}}{0.20 \text{ mol/L}} = 1.6 \text{ L/mol}\cdot\text{s}$$

58. Because $[B]_0 \gg [A]_0$, the B concentration is essentially constant during this experiment, so rate = $k'[A]$ where $k' = k[B]^2$. For this experiment, the reaction is a pseudo-first-order reaction in A.

a. $\ln\left(\frac{[A]}{[A]_0}\right) = -k't, \quad \ln\left(\frac{3.8 \times 10^{-3} \text{ M}}{1.0 \times 10^{-2} \text{ M}}\right) = -k' \times 8.0 \text{ s}, \quad k' = 0.12 \text{ s}^{-1}$

For the reaction: $k' = k[B]^2, \quad k = 0.12 \text{ s}^{-1}/(3.0 \text{ mol/L})^2 = 1.3 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$

b. $t_{1/2} = \frac{\ln 2}{k'} = \frac{0.693}{0.12 \text{ s}^{-1}} = 5.8 \text{ s}$

c. $\ln\left(\frac{[A]}{1.0 \times 10^{-2} \text{ M}}\right) = -0.12 \text{ s}^{-1} \times 13.0 \text{ s}, \quad \frac{[A]}{1.0 \times 10^{-2}} = e^{-0.12(13.0)} = 0.21$

$$[A] = 2.1 \times 10^{-3} \text{ M}$$

d. $[A]_{\text{reacted}} = 0.010 \text{ M} - 0.0021 \text{ M} = 0.008 \text{ M}$

$$[C]_{\text{reacted}} = 0.008 \text{ M} \times \frac{2 \text{ mol C}}{1 \text{ mol A}} = 0.016 \text{ M} \approx 0.02 \text{ M}$$

$[C]_{\text{remaining}} = 2.0 \text{ M} - 0.02 \text{ M} = 2.0 \text{ M}$; as expected, the concentration of C basically remains constant during this experiment since $[C]_0 \gg [A]_0$.

59. For elementary reactions, the rate law can be written using the coefficients in the balanced equation to determine orders.

a. Rate = $k[\text{CH}_3\text{NC}]$

b. Rate = $k[\text{O}_3][\text{NO}]$

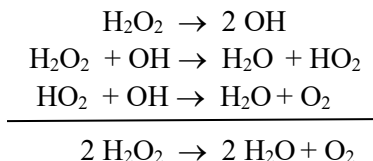
c. Rate = $k[\text{O}_3]$

d. Rate = $k[\text{O}_3][\text{O}]$

60. From experiment (Exercise 37), we know the rate law is Rate = $k[\text{H}_2\text{O}_2]$. A mechanism consists of a series of elementary reactions where the rate law for each step can be determined using the coefficients in the balanced equation for each respective step. For a plausible mechanism, the rate law derived from a mechanism must agree with the rate law determined from experiment. To derive the rate law from the mechanism, the rate of the reaction is assumed to equal the rate of the slowest step in the mechanism.

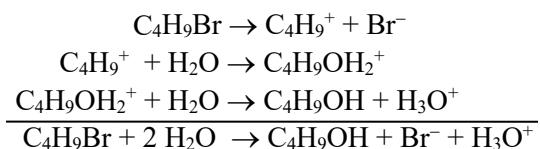
This mechanism will agree with the experimentally determined rate law only if step 1 is the slow step (called the rate-determining step). If step 1 is slow, then Rate = $k[\text{H}_2\text{O}_2]^2$ which agrees with experiment.

Another important property of a mechanism is that the sum of all steps must give the overall balanced equation. Summing all steps gives:



61. A mechanism consists of a series of elementary reactions in which the rate law for each step can be determined using the coefficients in the balanced equations. For a plausible mechanism, the rate law derived from a mechanism must agree with the rate law determined from experiment. To derive the rate law from the mechanism, the rate of the reaction is assumed to equal the rate of the slowest step in the mechanism.

Because step 1 is the rate-determining step, the rate law for this mechanism is $\text{Rate} = k[\text{C}_4\text{H}_9\text{Br}]$. To get the overall reaction, we sum all the individual steps of the mechanism. Summing all steps gives:

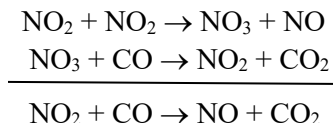


Intermediates in a mechanism are species that are neither reactants nor products but that are formed and consumed during the reaction sequence. The intermediates for this mechanism are C_4H_9^+ and $\text{C}_4\text{H}_9\text{OH}_2^+$.

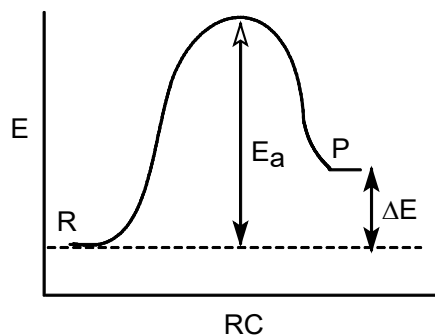
62. Because the rate of the slowest elementary step equals the rate of a reaction:

$$\text{Rate} = \text{rate of step 1} = k[\text{NO}_2]^2$$

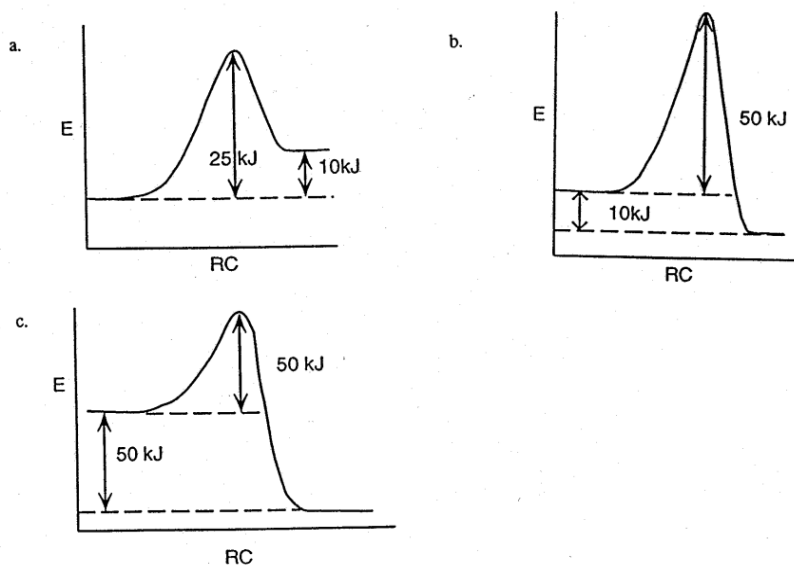
The sum of all steps in a plausible mechanism must give the overall balanced reaction. Summing all steps gives:



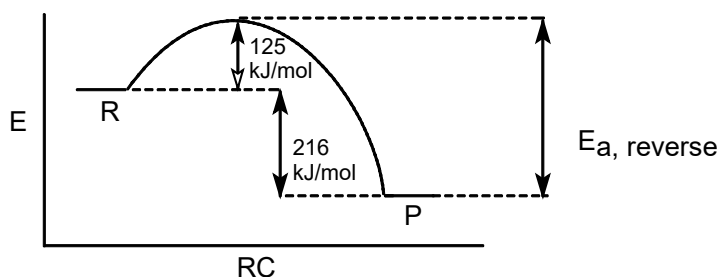
63. In the following plot, R = reactants, P = products, E_a = activation energy, and RC = reaction coordinate, which is the same as reaction progress. Note for this reaction that ΔE is positive because the products are at a higher energy than the reactants.



64. 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. RC = reaction coordinate, which is the same as reaction progress.



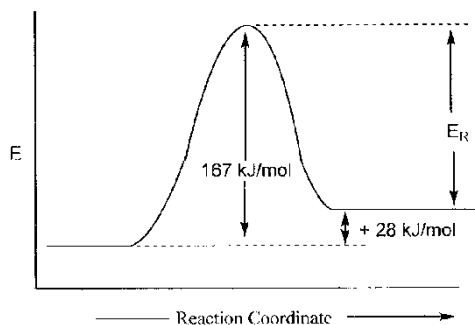
65.



The activation energy for the reverse reaction is:

$$E_{a, \text{ reverse}} = 216 \text{ kJ/mol} + 125 \text{ kJ/mol} = 341 \text{ kJ/mol}$$

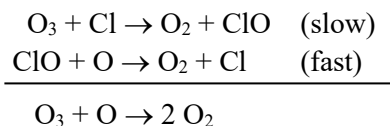
66.



The activation energy for the reverse reaction is E_R in the diagram.

$$E_R = 167 - 28 = 139 \text{ kJ/mol}$$

76. The mechanism for the chlorine catalyzed destruction of ozone is:



Because the chlorine atom-catalyzed reaction has a lower activation energy, the Cl-catalyzed rate is faster. Hence Cl is a more effective catalyst. Using the activation energy, we can estimate the efficiency that Cl atoms destroy ozone compared to NO molecules (see Exercise 75c).

$$\text{At } 25^\circ\text{C: } \frac{k_{\text{Cl}}}{k_{\text{NO}}} = \exp \left[\frac{-E_a(\text{Cl})}{RT} + \frac{E_a(\text{NO})}{RT} \right] = \exp \left[\frac{(-2100 + 11,900) \text{ J/mol}}{(8.3145 \times 298) \text{ J/mol}} \right] = e^{3.96} = 52$$

At 25°C , the Cl-catalyzed reaction is roughly 52 times faster than the NO-catalyzed reaction, assuming the frequency factor A is the same for each reaction.

98. Rate = $k[\text{DNA}]^x[\text{CH}_3\text{I}]^y$; comparing the second and third experiments:

$$\frac{1.28 \times 10^{-3}}{6.40 \times 10^{-4}} = \frac{k(0.200)^x(0.200)^y}{k(0.100)^x(0.200)^y}, \quad 2.00 = 2.00^x, \quad x = 1$$

Comparing the first and second experiments:

$$\frac{6.40 \times 10^{-4}}{3.20 \times 10^{-4}} = \frac{k(0.100)(0.200)^y}{k(0.100)(0.100)^y}, \quad 2.00 = 2.00^y, \quad y = 1$$

The rate law is Rate = $k[\text{DNA}][\text{CH}_3\text{I}]$.

Mechanism I is possible because the derived rate law from the mechanism (Rate = $k[\text{DNA}][\text{CH}_3\text{I}]$) agrees with the experimentally determined rate law. The derived rate law for Mechanism II will equal the rate of the slowest step. This is step 1 in the mechanism giving a derived rate law that is Rate = $k[\text{CH}_3\text{I}]$. Because this rate law does not agree with experiment, Mechanism II would not be a possible mechanism for the reaction.

105. Rate = $k[\text{I}^-]^x[\text{OCl}^-]^y[\text{OH}^-]^z$; comparing the first and second experiments:

$$\frac{18.7 \times 10^{-3}}{9.4 \times 10^{-3}} = \frac{k(0.0026)^x(0.012)^y(0.10)^z}{k(0.0013)^x(0.012)^y(0.10)^z}, \quad 2.0 = 2.0^x, \quad x = 1$$

Comparing the first and third experiments:

$$\frac{9.4 \times 10^{-3}}{4.7 \times 10^{-3}} = \frac{k(0.0013)(0.012)^y(0.10)^z}{k(0.0013)(0.0060)^y(0.10)^z}, \quad 2.0 = 2.0^y, \quad y = 1$$

Comparing the first and sixth experiments:

$$\frac{4.8 \times 10^{-3}}{9.4 \times 10^{-3}} = \frac{k(0.0013)(0.012)(0.20)^z}{k(0.0013)(0.012)(0.10)^z}, \quad 1/2 = 2.0^z, \quad z = -1$$

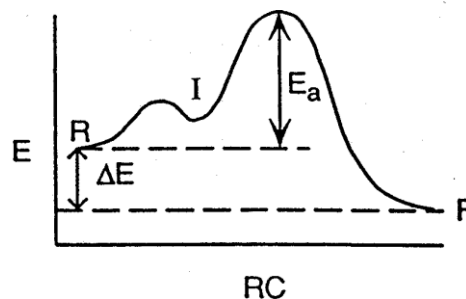
Rate = $\frac{k[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$; the presence of OH^- decreases the rate of the reaction.

For the first experiment:

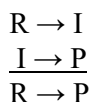
$$\frac{9.4 \times 10^{-3} \text{ mol}}{\text{L s}} = k \frac{(0.0013 \text{ mol/L})(0.012 \text{ mol/L})}{(0.10 \text{ mol/L})}, \quad k = 60.3 \text{ s}^{-1} = 60. \text{ s}^{-1}$$

For all experiments, $k_{\text{mean}} = 60. \text{ s}^{-1}$.

108. On the energy profile to the right, R = reactants, P = products, E_a = activation energy, ΔE = overall energy change for the reaction, I = intermediate, and RC = reaction coordinate, which is the same as reaction progress. For answers a-d, see plot to the right.



e. This is a two-step reaction since an intermediate plateau appears between the reactant and the products. This plateau represents the energy of the intermediate. The general reaction mechanism for this reaction is:



In a mechanism, the rate of the slowest step determines the rate of the reaction. The activation energy for the slowest step will be the largest energy barrier that the reaction must overcome. Since the second hump in the diagram is at the highest energy, the second step has the largest activation energy and will be the rate-determining step (the slow step).