

The second experimental method utilizes the fact that the integrated rate laws can be put in the form of a straight-line equation. Concentration versus time data are collected for a reactant as a reaction is run. These data are then manipulated and plotted to see which manipulation gives a straight line. From the straight-line plot we get the order of the reactant, and the slope of the line is mathematically related to  $k$ , the rate constant.

15. The average rate decreases with time because the reverse reaction occurs more frequently as the concentration of products increase. Initially, with no products present, the rate of the forward reaction is at its fastest, but as time goes on, the rate gets slower and slower since products are converting back into reactants. The instantaneous rate will also decrease with time. The only rate that is constant is the initial rate. This is the instantaneous rate taken at  $t \approx 0$ . At this time, the amount of products is insignificant, and the rate of the reaction only depends on the rate of the forward reaction.

16. The most common method to experimentally determine the differential rate law is the method of initial rates. Once the differential rate law is determined experimentally, the integrated rate law can be derived. However, sometimes it is more convenient and more accurate to collect concentration versus time data for a reactant. When this is the case, then we do "proof" plots to determine the integrated rate law. Once the integrated rate law is determined, the differential rate law can be determined. Either experimental procedure allows determination of both the integrated and the differential rate law; and which rate law is determined by experiment and which is derived is usually decided by which data are easiest and most accurately collected.

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

The rate doubles as the concentration quadruples:

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

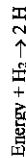
The order is  $1/2$  (the square root of the concentration of reactant).

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  $\text{H}_2$  and  $\text{O}_2$  molecules at room temperature do not have sufficient kinetic energy to form hydrogen atoms and initiate the reaction.

19. Two reasons are:

## CHAPTER 12

### CHEMICAL KINETICS

#### Questions

10. a. Activation energy and  $\Delta E$  are independent of each other. Activation energy depends on the path reactants take to convert to products. The overall energy change  $\Delta E$  only depends on the initial and final energy states of the reactants and products.  $\Delta E$  is path-independent.
- b. The rate law can only be determined from experiment, not from the overall balanced reaction.
- c. Most reactions occur by a series of steps. The rate of the reaction is determined by the rate of the slowest step in the mechanism.

11. In a unimolecular reaction, a single reactant molecule decomposes to products. In a bimolecular reaction, two molecules collide to give products. The probability of the simultaneous collision of three molecules with enough energy and the proper orientation is very small, making termolecular steps very unlikely.

12. a.  $T_2 > T_1$ ; as temperature increases, the distribution of collision energies shifts to the right. That is, as temperature increases, there are fewer collision energies with small energies and more collisions with large energies.

b. As temperature increases, more of the collisions have the required activation energy necessary to convert reactants into products. Hence, the rate of the reaction increases with increasing temperature.

13. All of 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  $\text{O}_2$  or  $\text{NO}$  does not affect the value of  $k$ , but it does increase the rate of the reaction because both concentrations appear in the rate law.

14. One experimental method to determine rate laws is the method of initial rates. Several experiments are carried out using different initial concentrations of reactants, and the initial rate is determined for each experiment. The results are then compared to see how the initial rate depends on the initial concentrations. This allows the orders in the rate law to be determined. The value of the rate constant is determined from the experiments once the orders are known.

- (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. This is why the catalyzed pathway is faster.
- b.  $\Delta E_1$  represents the activation energy for the uncatalyzed pathway.
- c.  $\Delta E_2$  represents the energy difference between the reactants and products. Note that  $\Delta E_2$  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.

21. Enzymes are very efficient catalysts. As is true for all catalysts, enzymes speed up a reaction by providing an alternative pathway for reactants to convert to products. This alternative pathway has a smaller activation energy and hence, a faster rate. Also true is that catalysts are not used up in the overall chemical reaction. Once an enzyme comes in contact with the correct reagent, the chemical reaction quickly occurs, and the enzyme is then free to catalyze another reaction. Because of the efficiency of the reaction step, only a relatively small amount of enzyme is needed to catalyze a specific reaction, no matter how complex the reaction.
22. The slope of the  $\ln k$  versus  $1/T$  plot (with temperature in Kelvin) is equal to  $-E_a/R$ . Because  $E_a$  for the catalyzed reaction will be smaller than  $E_a$  for the uncatalyzed reaction, the slope of the catalyzed plot should be less negative.

### Exercises

#### Reaction Rates

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.

$$\text{Rate} = -\frac{\Delta[PH_3]}{\Delta t} = \frac{-(-0.048 \text{ mol}/2.0 \text{ L})}{s} = 2.4 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

$$\frac{\Delta[P_4]}{\Delta t} = -\frac{1}{4} \frac{\Delta[PH_3]}{\Delta t} = 2.4 \times 10^{-3} / 4 = 6.0 \times 10^{-4} \text{ mol/L}\cdot\text{s}$$

$$\frac{\Delta[H_2]}{\Delta t} = -\frac{6}{4} \frac{\Delta[PH_3]}{\Delta t} = 6(2.4 \times 10^{-3}) / 4 = 3.6 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

24. Using the coefficients in the balanced equation to relate the rates:

$$\frac{\Delta[H_2]}{\Delta t} = 3 \frac{\Delta[N_2]}{\Delta t} \quad \text{and} \quad \frac{\Delta[NH_3]}{\Delta t} = -2 \frac{\Delta[N_2]}{\Delta t}$$

$$\text{So: } -\frac{1}{3} \frac{\Delta[H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[NH_3]}{\Delta t} \quad \text{or} \quad \frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta[H_2]}{\Delta t}$$

Ammonia is produced at a rate equal to 2/3 of the rate of consumption of hydrogen.

$$25. \quad \text{a. Average rate} = \frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500 \text{ M} - 1.000 \text{ M})}{(2.16 \times 10^4 \text{ s} - 0)} = 2.31 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

From the coefficients in the balanced equation:

$$\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[H_2O_2]}{\Delta t} = 1.16 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

$$b. \quad -\frac{\Delta[H_2O_2]}{\Delta t} = \frac{-(0.250 - 0.500) \text{ M}}{(4.32 \times 10^4 - 2.16 \times 10^4) \text{ s}} = 1.16 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

$$\frac{\Delta[O_2]}{\Delta t} = 1/2 (1.16 \times 10^{-5}) = 5.80 \times 10^{-6} \text{ mol/L}\cdot\text{s}$$

Notice that as time goes on in a reaction, the average rate decreases.

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  $2A + 3B \rightarrow 4C$ .

27. a. The units for rate are always mol/L·s. b. Rate = k; k must have units of mol/L·s.

$$c. \quad \text{Rate} = k[A], \quad \frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)$$

$$d. \quad \text{Rate} = k[A]^2, \quad \frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^2$$

k must have units of  $\text{s}^{-1}$ . k must have units of  $\text{L}/\text{mol}\cdot\text{s}$ .

$$e. \quad \text{L}^2/\text{mol}^2\cdot\text{s}$$

$$28. \quad \text{Rate} = k[C]^{1/2}[CHCl_3], \quad \frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^{1/2} \left( \frac{\text{mol}}{\text{L}} \right); \quad k \text{ must have units of } \text{L}^{1/2}/\text{mol}^{1/2}\cdot\text{s}$$

### Rate Laws from Experimental Data: Initial Rates Method

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  $\text{Cl}_2$ . Or mathematically,  $\text{Rate} = k[\text{NO}]^n[\text{Cl}_2]^m$ .

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

We can get the dependence on  $\text{NO}$  from the second and third experiments. Here, as the  $\text{NO}$  concentration doubles ( $\text{Cl}_2$  concentration is constant), the rate increases by a factor of four. Thus the reaction is second order with respect to  $\text{NO}$ . Or mathematically:

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

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:

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

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  $k_{\text{mean}} = 1.8 \times 10^2 \text{ L}^2/\text{mol}^2 \cdot \text{min}$ .

30. a.  $\text{Rate} = k[\Gamma][\text{S}_2\text{O}_8^{2-}]^x$ ;  $\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.040)^x(0.040)^y}$ ,  $2.00 = 2.0^x$ ,  $x = 1$

$$\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)(0.040)^y}{k(0.080)(0.020)^y}, \quad 2.00 = 2.0^y, \quad y = 1; \quad \text{Rate} = k[\Gamma][\text{S}_2\text{O}_8^{2-}]$$

- b. For the first experiment:

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

Each of the other experiments also gives  $k = 3.9 \times 10^{-3} \text{ L/mol} \cdot \text{s}$ , so  $k_{\text{mean}} = 3.9 \times 10^{-3} \text{ L/mol} \cdot \text{s}$ .

31. a.  $\text{Rate} = k[\text{NO}]^n$ ; using experiments two and three:

$$\frac{2.66 \times 10^4}{6.64 \times 10^3} = \frac{k(2.0 \times 10^{16})^n}{k(1.0 \times 10^{16})^n}, \quad 4.01 = 2.0^n, \quad n = 2; \quad \text{Rate} = k[\text{NO}]^2$$

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

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

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

32.  $\text{Rate} = k[\text{N}_2\text{O}_5]^x$ ; the rate laws for the first two experiments are:

$$2.26 \times 10^{-3} = k(0.190)^x \quad \text{and} \quad 8.90 \times 10^{-4} = k(0.0750)^x$$

Dividing the two rate laws:  $2.54 = \frac{(0.190)^x}{(0.0750)^x} = (2.53)^x$ ,  $x = 1$ ;  $\text{Rate} = k[\text{N}_2\text{O}_5]$

$$k = \frac{\text{Rate}}{[\text{N}_2\text{O}_5]} = \frac{8.90 \times 10^{-4} \text{ mol/L} \cdot \text{s}}{0.0750 \text{ mol/L}} = 1.19 \times 10^{-2} \text{ s}^{-1}$$

The other experiments give similar values for  $k$ .  $k_{\text{mean}} = 1.19 \times 10^{-2} \text{ s}^{-1}$

33. a.  $\text{Rate} = k[\Gamma][\text{OCl}\Gamma]^y$ ;  $\frac{7.91 \times 10^{-2}}{3.95 \times 10^{-2}} = \frac{k(0.12)^y(0.18)^y}{k(0.060)^y(0.18)^y} = 2.0^y$ ,  $2.00 = 2.0^y$ ,  $y = 1$

$$\frac{3.95 \times 10^{-2}}{9.88 \times 10^{-3}} = \frac{k(0.060)(0.18)^y}{k(0.030)(0.090)^y}, \quad 4.00 = 2.0 \times 2.0^y, \quad 2.0 = 2.0^y, \quad y = 1$$

$$\text{Rate} = k[\Gamma][\text{OCl}\Gamma]$$

- b. From the first experiment:  $\frac{7.91 \times 10^{-2} \text{ mol}}{\text{L} \cdot \text{s}} = k \left( \frac{0.12 \text{ mol}}{\text{L}} \right) \left( \frac{0.18 \text{ mol}}{\text{L}} \right)$ ;  $k = 3.7 \text{ L/mol} \cdot \text{s}$

All four experiments give the same value of  $k$  to two significant figures.

- c.  $\text{Rate} = \frac{3.7 \text{ L}}{\text{mol} \cdot \text{s}} \times \frac{0.15 \text{ mol}}{\text{L}} \times \frac{0.15 \text{ mol}}{\text{L}} = 0.083 \text{ mol/L} \cdot \text{s}$

34.  $\text{Rate} = k[\text{NO}]^x[\text{O}_2]^y$ ; 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  $\text{NO}$  ( $3^2 = 9$ ). The order of  $\text{O}_2$  is more difficult to determine. Comparing the second and third experiments:

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

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

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

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

$$k = 2.00 \times 10^{-38} \text{ cm}^6/\text{molecules}^3\text{s} = k_{\text{mean}}$$

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

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

35. a. Rate =  $k[\text{Hb}][\text{CO}]^y$

Comparing the first two experiments,  $[\text{CO}]$  is unchanged,  $[\text{Hb}]$  doubles, and the rate doubles. Therefore,  $x = 1$ , and the reaction is first order in Hb. Comparing the second and third experiments,  $[\text{Hb}]$  is unchanged,  $[\text{CO}]$  triples, and the rate triples. Therefore,  $y = 1$ , and the reaction is first order in CO.

- b. Rate =  $k[\text{Hb}][\text{CO}]$

- c. From the first experiment:

$$0.619 \mu\text{mol/L}\cdot\text{s} = k(2.21 \mu\text{mol/L})(1.00 \mu\text{mol/L}), k = 0.280 \text{ L}/\mu\text{mol}\cdot\text{s}$$

The second and third experiments give similar  $k$  values, so  $k_{\text{mean}} = 0.280 \text{ L}/\mu\text{mol}\cdot\text{s}$

- d. Rate =  $k[\text{Hb}][\text{CO}] = \frac{0.280 \text{ L}}{\mu\text{mol}\cdot\text{s}} \times \frac{3.36 \mu\text{mol}}{\text{L}} \times \frac{2.40 \mu\text{mol}}{\text{L}} = 2.26 \mu\text{mol/L}\cdot\text{s}$

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

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

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

Comparing the second and third experiments:

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

$$\text{Dividing: } 2.00 = \frac{(0.100)^y}{(0.0500)^y} = 2.00^y, y = 1$$

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

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

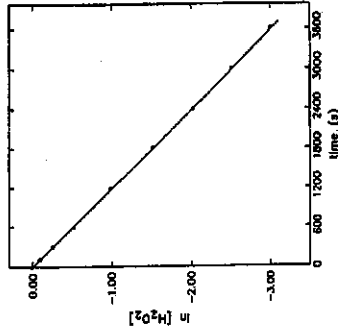
$k_{\text{mean}}$

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

### Integrated Rate Laws

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 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:

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

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:

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

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

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

- c.  $2.50 \times 10^{-3} \text{ M}$  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:

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

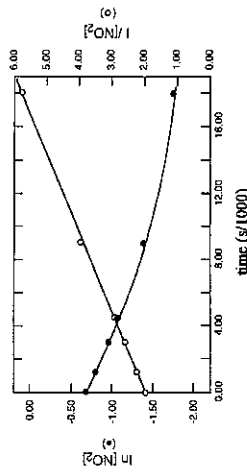
Or we can use the integrated rate law:

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

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

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



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

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  $1/[\text{NO}_2]_0 = 1/(0.500 \text{ M}) = 2.00 \text{ M}^{-1}$ .

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

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

40.

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

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

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

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

Note: We could have used the integrated rate law to solve for  $t_{1/2}$ , where  $[A] = (2.80 \times 10^{-3}/2) \text{ mol/L}$ .

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

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

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

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: 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.  $[\text{C}_2\text{H}_5\text{OH}] = -kt + [\text{C}_2\text{H}_5\text{OH}]_0$ ,  $0 \text{ mol/L} = -(4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s})t + 1.25 \times 10^{-2} \text{ mol/L}$
- $$t = \frac{1.25 \times 10^{-2} \text{ mol/L}}{4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s}} = 313 \text{ s}$$

42. From the data, the pressure of  $\text{C}_2\text{H}_5\text{OH}$  decreases at a constant rate of 13 torr for every 100. s. Because the rate of disappearance of  $\text{C}_2\text{H}_5\text{OH}$  is not dependent on concentration, the reaction is zero order in  $\text{C}_2\text{H}_5\text{OH}$ .

$$k = \frac{13 \text{ torr}}{100. \text{ s}} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.7 \times 10^{-4} \text{ atm/s}$$

The rate law and integrated rate law are:

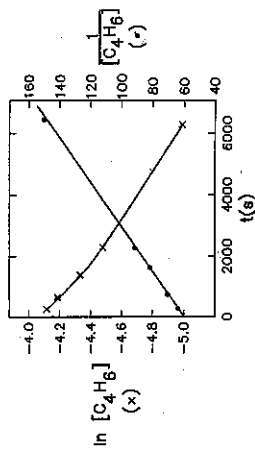
$$\text{Rate} = k = 1.7 \times 10^{-4} \text{ atm/s}; P_{\text{C}_2\text{H}_5\text{OH}} = -kt + 250. \text{ torr} \left( \frac{1 \text{ atm}}{760 \text{ torr}} \right) = -kt + 0.329 \text{ atm}$$

$$\text{At } 900. \text{ s: } P_{\text{C}_2\text{H}_5\text{OH}} = -1.7 \times 10^{-4} \text{ atm/s} \times 900. \text{ s} + 0.329 \text{ atm} = 0.176 \text{ atm} = 0.18 \text{ atm} = 130 \text{ torr}$$

43. The first assumption to make is that the reaction is first order. For a first-order reaction, a graph of  $\ln[\text{C}_4\text{H}_6]$  versus  $t$  should yield a straight line. If this isn't linear, then try the second-order plot of  $1/[\text{C}_4\text{H}_6]$  versus  $t$ . The data and the plots follow:

Time	195	604	1246	2180	6210 s
$[\text{C}_4\text{H}_6]$	$1.6 \times 10^{-2}$	$1.5 \times 10^{-2}$	$1.3 \times 10^{-2}$	$1.1 \times 10^{-2}$	$0.68 \times 10^{-2} \text{ M}$
$\ln[\text{C}_4\text{H}_6]$	-4.14	-4.20	-4.34	-4.51	-4.99
$1/[\text{C}_4\text{H}_6]$	62.5	66.7	76.9	90.9	$147 \text{ M}^{-1}$

Note: To reduce round-off error, we carried extra significant figures in the data points.



The natural log plot is not linear, so the reaction is not first order. Because the second-order plot of  $1/[\text{C}_4\text{H}_6]$  versus  $t$  is linear, we can conclude that the reaction is second order in butadiene. The rate law is:

$$\text{Rate} = k[\text{C}_4\text{H}_6]^2$$

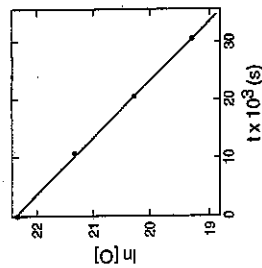
For a second-order reaction, the integrated rate law is  $\frac{1}{[\text{C}_4\text{H}_6]} = kt + \frac{1}{[\text{C}_4\text{H}_6]_0}$ .

The slope of the straight line equals the value of the rate constant. Using the points on the line at 1000. and 6000. s:

$$k = \text{slope} = \frac{144 \text{ L/mol} - 73 \text{ L/mol}}{6000. \text{ s} - 1000. \text{ s}} = 1.4 \times 10^{-2} \text{ L/mol}\cdot\text{s}$$

44. a. First, assume the reaction to be first order with respect to O. Hence a graph of  $\ln[\text{O}]$  versus  $t$  would be linear if the reaction is first order.

$t$ (s)	$[\text{O}]$ (atoms/cm <sup>3</sup> )	$\ln[\text{O}]$
0	$5.0 \times 10^9$	22.33
$10. \times 10^{-3}$	$1.9 \times 10^9$	21.37
$20. \times 10^{-3}$	$6.8 \times 10^8$	20.34
$30. \times 10^{-3}$	$2.5 \times 10^8$	19.34



Because the graph is linear, we can conclude the reaction is first order with respect to O.

- b. The overall rate law is  $\text{Rate} = k[\text{NO}_2][\text{O}]$ .

Because  $\text{NO}_2$  was in excess, its concentration is constant. Thus, for this experiment, the rate law is  $\text{Rate} = k'[\text{O}]$ , where  $k' = k[\text{NO}_2]$ . In a typical first-order plot, the slope equals  $-k$ . For this experiment, the slope equals  $-k' = -k[\text{NO}_2]$ . From the graph:

$$\text{slope} = \frac{19.34 - 22.23}{(3.0 \times 10^{-3} - 0)\text{s}} = -1.0 \times 10^2 \text{ s}^{-1}, \quad k' = -\text{slope} = 1.0 \times 10^2 \text{ s}^{-1}$$

To determine  $k$ , the actual rate constant:

$$k' = k[\text{NO}_2], \quad 1.0 \times 10^2 \text{ s}^{-1} = k(1.0 \times 10^{15} \text{ molecules/cm}^3)$$

$$k = 1.0 \times 10^{-11} \text{ cm}^3/\text{molecules}\cdot\text{s}$$

45. Because the  $1/[A]$  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  $1/[A]_0$ . Extending the plot, the y intercept will be about 10, so  $1/10 = 0.1 \text{ M} = [A]_0$ .

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

48. a. The integrated rate law for this zero-order reaction is  $[\text{HI}] = -kt + [\text{HI}]_0$ .

$$[\text{HI}] = -kt + [\text{HI}]_0, \quad [\text{HI}] = -\left(\frac{1.20 \times 10^{-4} \text{ mol}}{\text{L}\cdot\text{s}}\right) \times \left(25 \text{ min} \times \frac{60 \text{ s}}{\text{min}}\right) + \frac{0.250 \text{ mol}}{\text{L}}$$

$$[\text{HI}] = -0.18 \text{ mol/L} + 0.250 \text{ mol/L} = 0.07 \text{ M}$$

- b.  $[\text{HI}] = 0 = -kt + [\text{HI}]_0$ ,  $kt = [\text{HI}]_0$ ,  $t = \frac{[\text{HI}]_0}{k}$

$$t = \frac{0.250 \text{ mol/L}}{1.20 \times 10^{-4} \text{ mol/L}\cdot\text{s}} = 2080 \text{ s} = 34.7 \text{ min}$$

49. If  $[A]_0 = 100.0$ , then after 65 s, 45.0% of A has reacted, or  $[A] = 55.0$ . For first order reactions:

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt, \quad \ln\left(\frac{55.0}{100.0}\right) = -k(65 \text{ s}), \quad k = 9.2 \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{9.2 \times 10^{-3} \text{ s}^{-1}} = 75 \text{ s}$$

50. a. When a reaction is 75.0% complete (25.0% of reactant remains), this represents two half-lives ( $100\% \rightarrow 50\% \rightarrow 25\%$ ). The first-order half-life expression is  $t_{1/2} = (\ln 2)/k$ . Because there is no concentration dependence for a first-order half-life, 320. s = two half-lives,  $t_{1/2} = 320.72 = 160$ . s. This is both the first half-life, the second half-life, etc.

- b.  $t_{1/2} = \frac{\ln 2}{k}$ ,  $k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{160. \text{ s}} = 4.33 \times 10^{-3} \text{ s}^{-1}$

At 90.0% complete, 10.0% of the original amount of the reactant remains, so  $[A] = 0.100[A]_0$ .

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt, \quad \ln\left(\frac{0.100[A]_0}{[A]_0}\right) = -(4.33 \times 10^{-3} \text{ s}^{-1})t, \quad t = \frac{\ln(0.100)}{-4.33 \times 10^{-3} \text{ s}^{-1}} = 532 \text{ s}$$

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

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

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

52.  $\ln\left(\frac{[A]}{[A]_0}\right) = -kt$ ;  $k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{56.0 \text{ days}} = 0.0124 \text{ d}^{-1}$

$$\ln\left(\frac{1.41 \times 10^{-7} \text{ mol/L}}{8.75 \times 10^{-5} \text{ mol/L}}\right) = -(0.0124 \text{ d}^{-1})t, \quad t = 519 \text{ days}$$

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.

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

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

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

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

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

56. The consecutive half-life values of 24 hours, then 12 hours, show a direct relationship with concentration; as the concentration decreases, the half-life decreases. Assuming the drug reaction is either zero, first, or second order, only a zero order reaction shows this direct relationship between half-life and concentration. Therefore, assume the reaction is zero order in the drug.

$$t_{1/2} = \frac{[A]_0}{2k}, \quad k = \frac{[A]_0}{2t_{1/2}} = \frac{2.0 \times 10^{-3} \text{ mol/L}}{2(24 \text{ h})} = 4.2 \times 10^{-5} \text{ mol/L}\cdot\text{h}$$

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

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

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

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

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

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

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

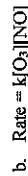
M

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



### Reaction Mechanisms

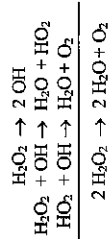
59. For elementary reactions, the rate law can be written using the coefficients in the balanced equation to determine orders.



60. From experiment (Exercise 37), we know the rate law is  $\text{Rate} = k[\text{H}_2\text{O}_2]$ . 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.

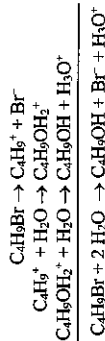
This mechanism will agree with the experimentally determined rate law only if step 1 is the slow step (called the rate-determining step). If step 1 is slow, then  $\text{Rate} = k[\text{H}_2\text{O}_2]$ , which agrees with experiment.

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:

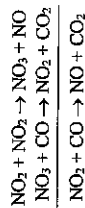


Intermediates in a mechanism are species that are neither reactants nor products but that are formed and consumed during the reaction sequence. The intermediates for this mechanism are  $\text{C}_4\text{H}_9^+$  and  $\text{C}_4\text{H}_9\text{OH}_2^+$ .

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

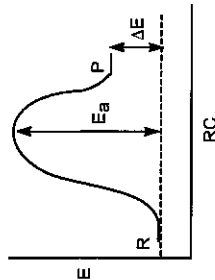
$$\text{Rate} = \text{rate of step 1} = k[\text{NO}_2]^2$$

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

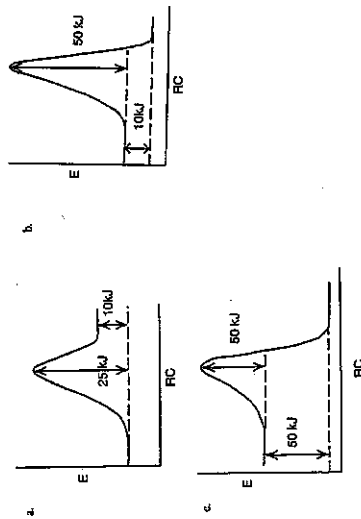


### Temperature Dependence of Rate Constants and the Collision Model

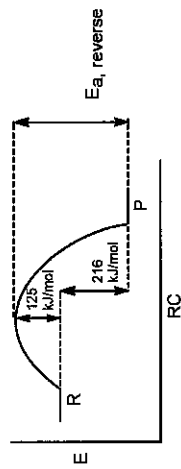
63. In the following plot, R = reactants, P = products,  $E_a$  = activation energy, and RC = reaction coordinate, which is the same as reaction progress. Note for this reaction that  $\Delta E$  is positive because the products are at a higher energy than the reactants.



64. When  $\Delta E$  is positive, the products are at a higher energy relative to reactants, and when  $\Delta E$  is negative, the products are at a lower energy relative to reactants. RC = reaction coordinate, which is the same as reaction progress.



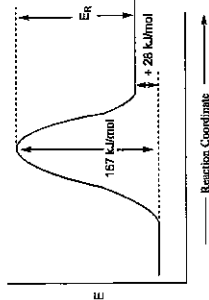
65.



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.



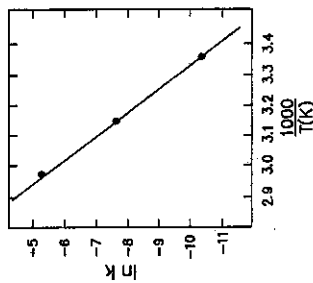
The activation energy for the reverse reaction is  $E_R$  in the diagram.

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

67.

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  $\ln k$  versus  $1/T$  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 extra significant figures in the following  $\ln k$  values in order to reduce round off error.

T (K)	1/T (K <sup>-1</sup> )	k (s <sup>-1</sup> )	ln k
338	$2.96 \times 10^{-3}$	$4.9 \times 10^{-3}$	-5.32
318	$3.14 \times 10^{-3}$	$5.0 \times 10^{-4}$	-7.60
298	$3.36 \times 10^{-3}$	$3.5 \times 10^{-5}$	-10.26



$$\text{Slope} = \frac{-10.76 - (-5.85)}{3.40 \times 10^{-3} - 3.00 \times 10^{-3}} = -1.2 \times 10^4 \text{ K} = -E_a/R$$

$$E_a = -\text{slope} \times R = 1.2 \times 10^4 \text{ K} \times \frac{8.3145 \text{ J}}{\text{K mol}}, E_a = 1.0 \times 10^5 \text{ J/mol} = 1.0 \times 10^2 \text{ kJ/mol}$$

68. From the Arrhenius equation in logarithmic form ( $\ln k = -E_a/RT + \ln A$ ), a graph of  $\ln k$  versus  $1/T$  should yield a straight line with a slope equal to  $-E_a/R$  and a  $y$  intercept equal to  $\ln A$ .

$$\text{a. Slope} = -E_a/R, E_a = 1.10 \times 10^4 \text{ K} \times \frac{8.3145 \text{ J}}{\text{K mol}} = 9.15 \times 10^4 \text{ J/mol} = 91.5 \text{ kJ/mol}$$

b. The units for  $A$  are the same as the units for  $k$  (s<sup>-1</sup>).

$$y \text{ intercept} = \ln A, A = e^{33.5} = 3.54 \times 10^{14} \text{ s}^{-1}$$

$$\text{c. } \ln k = -E_a/RT + \ln A \text{ or } k = A \exp(-E_a/RT)$$

$$k = 3.54 \times 10^{14} \text{ s}^{-1} \times \exp\left(\frac{-9.15 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol} \times 298 \text{ K}}\right) = 3.24 \times 10^{-2} \text{ s}^{-1}$$

$$69. k = A \exp(-E_a/RT) \text{ or } \ln k = \frac{-E_a}{RT} + \ln A \text{ (the Arrhenius equation)}$$

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

$$\text{Let } k_1 = 3.52 \times 10^{-7} \text{ L/mol}\cdot\text{s}, T_1 = 555 \text{ K}, k_2 = ?, T_2 = 645 \text{ K}, E_a = 186 \times 10^3 \text{ J/mol}$$

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{1.86 \times 10^5 \text{ J/mol} \left( \frac{1}{555 \text{ K}} - \frac{1}{645 \text{ K}} \right)}{8.3145 \text{ J/K} \cdot \text{mol}} = 5.6$$

$$\frac{k_2}{3.52 \times 10^{-7}} = e^{5.6} = 270, \quad k_2 = 270(3.52 \times 10^{-7}) = 9.5 \times 10^{-5} \text{ L/mol}\cdot\text{s}$$

70. 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 is temperature independent.)

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

$$0.57 = \frac{E_a}{8.3145} (2.5 \times 10^{-4}), \quad E_a = 1.9 \times 10^4 \text{ J/mol} = 19 \text{ kJ/mol}$$

71.  $\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right); \quad \frac{k_2}{k_1} = 7.00, \quad T_1 = 295 \text{ K}, \quad E_a = 54.0 \times 10^3 \text{ J/mol}$

$$\ln(7.00) = \frac{5.4 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{295 \text{ K}} - \frac{1}{T_2} \right); \quad \frac{1}{T_2} - \frac{1}{295 \text{ K}} = \frac{1}{3.00 \times 10^{-4}}$$

$$\frac{1}{T_2} = 3.09 \times 10^{-3}, \quad T_2 = 324 \text{ K} = 51^\circ\text{C}$$

72.  $\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$ ; because the rate doubles,  $k_2 = 2k_1$ .

$$\ln(2.00) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}} \right); \quad E_a = 5.3 \times 10^4 \text{ J/mol} = 53 \text{ kJ/mol}$$

73.  $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$  should have the faster rate.  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  will be electrostatically attracted to each other;  $\text{Ce}^{4+}$  and  $\text{Hg}_2^{2+}$  will repel each other. The activation energy for the  $\text{Ce}^{4+}$  and  $\text{Hg}_2^{2+}$  reaction should be a larger quantity, making it the slower reaction.

74. Carbon cannot form the fifth bond necessary for the transition state because of the small atomic size of carbon and because carbon doesn't have low-energy d orbitals available to expand the octet.

### Catalysts

75. a. NO is the catalyst. NO is present in the first step of the mechanism on the reactant side, but it is not a reactant. NO is regenerated in the second step and does not appear in overall balanced equation.

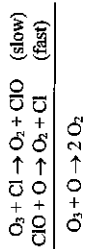
b.  $\text{NO}_2$  is an intermediate. Intermediates also never appear in the overall balanced equation. In a mechanism, intermediates always appear first on the product side, whereas catalysts always appear first on the reactant side.

c.  $k = A \exp(-E_a/RT); \quad \frac{k_{\text{cat}}}{k_{\text{un}}} = \frac{A \exp[-E_a(\text{cat})/RT]}{A \exp[-E_a(\text{un})/RT]} = \exp \left[ \frac{E_a(\text{un}) - E_a(\text{cat})}{RT} \right]$

$$\frac{k_{\text{cat}}}{k_{\text{un}}} = \exp \left( \frac{2100 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol} \times 298 \text{ K}} \right) = e^{0.85} = 2.3$$

The catalyzed reaction is approximately 2.3 times faster than the uncatalyzed reaction at  $25^\circ\text{C}$ .

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

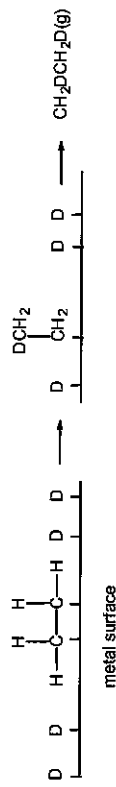


Because the chlorine atom-catalyzed reaction has a lower activation energy, the Cl-catalyzed rate is faster. Hence Cl is a more effective catalyst. Using the activation energy, we can estimate the efficiency that Cl atoms destroy ozone compared to NO molecules (see Exercise 75c).

$$\text{At } 25^\circ\text{C}: \quad \frac{k_{\text{Cl}}}{k_{\text{NO}}} = \exp \left[ \frac{-E_a(\text{Cl})}{RT} + \frac{E_a(\text{NO})}{RT} \right] = \exp \left[ \frac{(-2100 + 11,900) \text{ J/mol}}{(8.3145 \times 298) \text{ J/mol}} \right] = e^{3.56} = 52$$

At  $25^\circ\text{C}$ , 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.

77. The reaction at the surface of the catalyst is assumed to follow the steps:



Thus  $\text{CH}_2\text{D}-\text{CH}_2\text{D}$  should be the product. If the mechanism is possible, then the reaction must be:



If we got this product, then we could conclude that this is a possible mechanism. If we got some other product, for example,  $\text{CH}_3\text{CHD}_2$ , then we would conclude that the mechanism is wrong. Even though this mechanism correctly predicts the products of the reaction, we cannot say conclusively that this is the correct mechanism; we might be able to conceive of other mechanisms that would give the same products as our proposed one.

a. W because it has a lower activation energy than the Os catalyst.

- b.  $k_w = A_w \exp(-E_a(W)/RT)$ ;  $k_{uncat} = A_{uncat} \exp[-E_a(\text{uncat})/RT]$ ; assume  $A_w = A_{uncat}$ .

$$\frac{k_w}{k_{uncat}} = \exp\left[\frac{-E_a(W)}{RT} + \frac{E_a(\text{uncat})}{RT}\right]$$

$$\frac{k_w}{k_{uncat}} = \exp\left[\frac{-163,000 \text{ J/mol} + 335,000 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol} \times 298 \text{ K}}\right] = 1.41 \times 10^{30}$$

The W-catalyzed reaction is approximately  $10^{30}$  times faster than the uncatalyzed reaction.

- c. Because  $[H_2]$  is in the denominator of the rate law, the presence of  $H_2$  decreases the rate of the reaction. For the decomposition to occur,  $NH_3$  molecules must be adsorbed on the surface of the catalyst. If  $H_2$  is also adsorbed on the catalyst surface, then there are fewer sites for  $NH_3$  molecules to be adsorbed, and the rate decreases.

79. The rate depends on the number of reactant molecules adsorbed on the surface of the catalyst. This quantity is proportional to the concentration of reactant. However, when all the catalyst surface sites are occupied, the rate becomes independent of the concentration of reactant.

80. At high  $[S]$ , the enzyme is completely saturated with substrate. Once the enzyme is completely saturated, the rate of decomposition of ES can no longer increase, and the overall rate remains constant.

81. Assuming the catalyzed and uncatalyzed reactions have the same form and orders, and because concentrations are assumed equal, the rates will be equal when the  $k$  values are equal.

$$k = A \exp(-E_a/RT); k_{cat} = k_{un} \text{ when } E_{a,cat}/RT_{cat} = E_{a,un}/RT_{un}$$

$$\frac{4.20 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol} \times 293 \text{ K}} = \frac{7.00 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol} \times T_{un}}, T_{un} = 488 \text{ K} = 215^\circ\text{C}$$

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

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

$$\frac{\text{Rate}_{cat}}{\text{Rate}_{un}} = \frac{\Delta t_{un}}{\Delta t_{cat}} \text{ and } \frac{\text{rate}_{cat}}{\text{rate}_{un}} = \frac{k_{cat}}{k_{un}}$$

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

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

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

### Additional Exercises

83. Box a has 8  $NO_2$  molecules. Box b has 4  $NO_2$  molecules, and box c has 2  $NO_2$  molecules. Box b represents what is present after the first half-life of the reaction, and box c represents what is present after the second half-life.

- a. For first order kinetics,  $t_{1/2} = 0.693/k$ ; the half-life for a first order reaction is concentration independent. Therefore, the time for box c, the time it takes to go through two half-lives, will be  $10 + 10 = 20$  minutes.

- b. For second order kinetics,  $t_{1/2} = 1/k[A]_0$ , the half-life for a second order reaction is inversely proportional to the initial concentration. So if the first half-life is 10 minutes, the second half-life will be 20 minutes. For a second order reaction, the time for box c will be  $10 + 20 = 30$  minutes.

- c. For zero order kinetics,  $t_{1/2} = [A]_0/2k$ ; the half-life for a zero order reaction is directly related to the initial concentration. So if this reaction was zero order, then the second half-life would decrease from 10 min to 5 min. The time for box c will be  $10 + 5 = 15$  minutes if the reaction is zero order.

84.  $\text{Rate} = k[H_2SeO_3]^x[H^+]^y[I^-]^z$ ; comparing the first and second experiments:

$$\frac{3.33 \times 10^{-7}}{1.66 \times 10^{-7}} = \frac{k(2.0 \times 10^{-4})^x(2.0 \times 10^{-2})^y(2.0 \times 10^{-2})^z}{k(1.0 \times 10^{-4})^x(2.0 \times 10^{-2})^y(2.0 \times 10^{-2})^z}, 2.01 = 2.0^x, x = 1$$

Comparing the first and fourth experiments:

$$\frac{6.66 \times 10^{-7}}{1.66 \times 10^{-7}} = \frac{k(1.0 \times 10^{-4})(4.0 \times 10^{-2})^y(2.0 \times 10^{-2})^z}{k(1.0 \times 10^{-4})(2.0 \times 10^{-2})^y(2.0 \times 10^{-2})^z}, 4.01 = 2.0^y, y = 2$$

Comparing the first and sixth experiments:

$$\frac{13.2 \times 10^{-7}}{1.66 \times 10^{-7}} = \frac{k(1.0 \times 10^{-4})(2.0 \times 10^{-2})^y(4.0 \times 10^{-2})^z}{k(1.0 \times 10^{-4})(2.0 \times 10^{-2})^y(2.0 \times 10^{-2})^z}$$

$$7.95 = 2.0^z, \log(7.95) = z \log(2.0), z = \frac{\log(7.95)}{\log(2.0)} = 2.99 \approx 3$$

$$\text{Rate} = k[H_2SeO_3][H^+]^3[I^-]^3$$

Experiment 1:

$$\frac{1.66 \times 10^{-7} \text{ mol}}{\text{L s}} = k \left( \frac{1.0 \times 10^{-4} \text{ mol}}{\text{L}} \right) \left( \frac{2.0 \times 10^{-2} \text{ mol}}{\text{L}} \right)^2 \left( \frac{2.0 \times 10^{-2} \text{ mol}}{\text{L}} \right)^3$$

$$k = 5.19 \times 10^5 \text{ L}^5/\text{mol}^5\text{s} = 5.2 \times 10^5 \text{ L}^5/\text{mol}^5\text{s} = k_{\text{mean}}$$

85. The integrated rate law for each reaction is:

$$\ln[A] = -4.50 \times 10^{-4} \text{ s}^{-1}(t) + \ln[A]_0 \quad \text{and} \quad \ln[B] = -3.70 \times 10^{-3} \text{ s}^{-1}(t) + \ln[B]_0$$

Subtracting the second equation from the first equation ( $\ln[A]_0 = \ln[B]_0$ ):

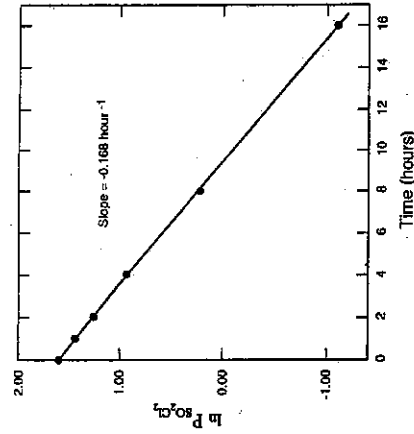
$$\ln[A] - \ln[B] = -4.50 \times 10^{-4}(t) + 3.70 \times 10^{-3}(t), \quad \ln\left(\frac{[A]}{[B]}\right) = 3.25 \times 10^{-3}(t)$$

$$\text{When } [A] = 4.00 [B], \quad \ln(4.00) = 3.25 \times 10^{-3}(t), \quad t = 427 \text{ s.}$$

86. The pressure of a gas is directly proportional to concentration. Therefore, we can use the pressure data to solve the problem because  $\text{Rate} = -\Delta[\text{SO}_2\text{Cl}_2]/\Delta t \propto -\Delta P_{\text{SO}_2\text{Cl}_2}/\Delta t$ .

Assuming a first order equation, the data and plot follow.

Time (hour)	0.00	1.00	2.00	4.00	8.00	16.00
$P_{\text{SO}_2\text{Cl}_2}$ (atm)	4.93	4.26	3.52	2.53	1.30	0.34
$\ln P_{\text{SO}_2\text{Cl}_2}$	1.595	1.449	1.258	0.928	0.262	-1.08



Because the  $\ln P_{\text{SO}_2\text{Cl}_2}$  versus time plot is linear, the reaction is first order in  $\text{SO}_2\text{Cl}_2$ .

a. Slope of  $\ln(P)$  versus  $t$  plot:  $-0.168 \text{ hour}^{-1} = -k$ ,  $k = 0.168 \text{ hour}^{-1} = 4.67 \times 10^{-5} \text{ s}^{-1}$

Because concentration units don't appear in first-order rate constants, this value of  $k$  determined from the pressure data will be the same as if concentration data in molarity units were used.

$$\text{b. } t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{0.168 \text{ h}^{-1}} = 4.13 \text{ hour}$$

$$\text{c. } \ln\left(\frac{P_{\text{SO}_2\text{Cl}_2}}{P_0}\right) = -kt = -0.168 \text{ h}^{-1}(20.0 \text{ h}) = -3.36, \quad \left(\frac{P_{\text{SO}_2\text{Cl}_2}}{P_0}\right) = e^{-3.36} = 3.47 \times 10^{-2}$$

Fraction remaining = 0.0347 = 3.47%

87. From 338 K data, a plot of  $\ln[\text{N}_2\text{O}_5]$  versus  $t$  is linear, and the slope =  $-4.86 \times 10^{-3}$  (plot not included). This tells us the reaction is first order in  $\text{N}_2\text{O}_5$  with  $k = 4.86 \times 10^{-3}$  at 338 K.

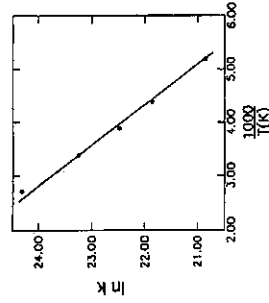
From 318 K data, the slope of  $\ln[\text{N}_2\text{O}_5]$  versus  $t$  plot is equal to  $-4.98 \times 10^{-4}$ , so  $k = 4.98 \times 10^{-4}$  at 318 K. We now have two values of  $k$  at two temperatures, so we can solve for  $E_a$ .

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right), \quad \ln\left(\frac{4.86 \times 10^{-3}}{4.98 \times 10^{-4}}\right) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{318 \text{ K}} - \frac{1}{338 \text{ K}} \right)$$

$$E_a = 1.0 \times 10^5 \text{ J/mol} = 1.0 \times 10^2 \text{ kJ/mol}$$

88. 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  $\ln k$  versus  $1/T$  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 <sup>-1</sup> )	k (L/mol*s)	ln k
195	$5.13 \times 10^{-3}$	$1.08 \times 10^8$	20.80
230	$4.35 \times 10^{-3}$	$2.95 \times 10^9$	21.81
260	$3.85 \times 10^{-3}$	$5.42 \times 10^9$	22.41
298	$3.36 \times 10^{-3}$	$12.0 \times 10^9$	23.21
369	$2.71 \times 10^{-3}$	$35.5 \times 10^9$	24.29



Using a couple of points on the plot:

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

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

89. To determine the rate of reaction, we need to calculate the value of the rate constant  $k$ . The activation energy data can be manipulated to determine  $k$ .

$$k = A e^{-E_a/RT} = 0.850 \text{ s}^{-1} \times \exp\left(\frac{-26.2 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol} \times 310.2 \text{ K}}\right) = 3.29 \times 10^{-5} \text{ s}^{-1}$$

Rate =  $k$ [acetylcholine receptor-toxin complex]

$$\text{Rate} = 3.29 \times 10^{-5} \text{ s}^{-1} \left(\frac{0.200 \text{ mol}}{\text{L}}\right) = 6.58 \times 10^{-6} \text{ mol/L} \cdot \text{s}$$

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

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

Comparing the first and second experiments:

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

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.

91. a. If the interval between flashes is 16.3 s, then the rate is:

$$1 \text{ flash}/16.3 \text{ s} = 6.13 \times 10^{-2} \text{ s}^{-1} = k$$

Interval	k	T
16.3 s	$6.13 \times 10^{-2} \text{ s}^{-1}$	21.0°C (294.2 K)
13.0 s	$7.69 \times 10^{-2} \text{ s}^{-1}$	27.8°C (301.0 K)

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right); \text{ solving using above data: } E_a = 2.5 \times 10^4 \text{ J/mol} = 25 \text{ kJ/mol}$$

$$\text{b. } \ln\left(\frac{k}{6.13 \times 10^{-2}}\right) = \frac{2.5 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{294.2 \text{ K}} - \frac{1}{303.2 \text{ K}}\right) = 0.30$$

$$k = e^{0.30} \times (6.13 \times 10^{-2}) = 8.3 \times 10^{-2} \text{ s}^{-1}; \text{ interval} = 1/k = 12 \text{ seconds.}$$

c. T	Interval	54-2(Intervals)
21.0°C	16.3 s	28°C
27.8°C	13.0 s	30°C
30.0°C	12 s	

This rule of thumb gives excellent agreement to two significant figures.

$$92. k = A \exp(-E_a/RT); \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{A_{\text{cat}} \exp(-E_{a,\text{cat}}/RT)}{A_{\text{uncat}} \exp(-E_{a,\text{uncat}}/RT)} = \exp\left(\frac{-E_{a,\text{cat}} + E_{a,\text{uncat}}}{RT}\right)$$

$$2.50 \times 10^3 = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \exp\left(\frac{-E_{a,\text{cat}} + 5.00 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol} \times 310. \text{ K}}\right)$$

$$\ln(2.50 \times 10^3) = 2.58 \times 10^3 \text{ J/mol} = -E_{a,\text{cat}} + 5.00 \times 10^4 \text{ J/mol}$$

$$E_{a,\text{cat}} = 5.00 \times 10^4 \text{ J/mol} - 2.02 \times 10^4 \text{ J/mol} = 2.98 \times 10^4 \text{ J/mol} = 29.8 \text{ kJ/mol}$$

93. a. Because  $[A]_0 \ll [B]_0$  or  $[C]_0$ , the B and C concentrations remain constant at 1.00 M for this experiment. Thus Rate =  $k[A]^2[B][C] = k'[A]^2$ , where  $k' = k[B][C]$ .

For this pseudo-second-order reaction:

$$\frac{1}{[A]} = k't + \frac{1}{[A]_0}, \frac{1}{3.26 \times 10^{-5} M} = k'(3.00 \text{ min}) + \frac{1}{1.00 \times 10^{-4} M}$$

$$k' = 6890 \text{ L/mol} \cdot \text{min} = 115 \text{ L/mol} \cdot \text{s}$$

$$k' = k[B][C], k = \frac{k'}{[B][C]} = \frac{115 \text{ L/mol} \cdot \text{s}}{(1.00 M)(1.00 M)} = 115 \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

- b. For this pseudo-second-order reaction:

$$\text{Rate} = k'[A]^2, t_{1/2} = \frac{1}{k'[A]_0} = \frac{1}{115 \text{ L/mol} \cdot \text{s}(1.00 \times 10^{-4} \text{ mol/L})} = 87.0 \text{ s}$$

$$\text{c. } \frac{1}{[A]} = k't + \frac{1}{[A]_0} = 115 \text{ L/mol} \cdot \text{s} \times 600. \text{ s} + \frac{1}{1.00 \times 10^{-4} \text{ mol/L}} = 7.90 \times 10^4 \text{ L/mol}$$

$$[A] = 1/7.90 \times 10^4 \text{ L/mol} = 1.27 \times 10^{-5} \text{ mol/L}$$

From the stoichiometry in the balanced reaction, 1 mol of B reacts with every 3 mol of A.

$$\text{Amount A reacted} = 1.00 \times 10^{-4} M - 1.27 \times 10^{-5} M = 8.7 \times 10^{-5} M$$

$$\text{Amount B reacted} = 8.7 \times 10^{-5} \text{ mol/L} \times \frac{1 \text{ mol B}}{3 \text{ mol A}} = 2.9 \times 10^{-5} M$$

$$[B] = 1.00 M - 2.9 \times 10^{-5} M = 1.00 M$$

As we mentioned in part a, the concentration of B (and C) remains constant because the A concentration is so small compared to the B (or C) concentration.

### ChemWork Problems

The answers to the problems 94-101 (or a variation to these problem) are found in OWL. These problems are also assignable in OWL.

### Challenge Problems

$$102. \quad -\frac{d[A]}{dt} = k[A]^3, \quad \int_{[A]_b}^{[A]_i} \frac{d[A]}{[A]^3} = -\int_0^t k \, dt$$

$$\int x^n dx = \frac{x^{n+1}}{n+1}; \text{ so, } -\frac{1}{2[A]^2} \Big|_{[A]_b}^{[A]_i} = -kt, \quad -\frac{1}{2[A]_i^2} + \frac{1}{2[A]_b^2} = -kt$$

For the half-life equation,  $[A]_i = 1/2[A]_b$ :

$$-\frac{1}{2\left(\frac{1}{2}[A]_b\right)^2} + \frac{1}{2[A]_b^2} = -kt_{1/2}, \quad -\frac{4}{2[A]_b^2} + \frac{1}{2[A]_b^2} = -kt_{1/2}$$

$$-\frac{3}{2[A]_b^2} = -kt_{1/2}, \quad t_{1/2} = \frac{3}{2[A]_b^2} k$$

The first half-life is  $t_{1/2} = 40. \text{ s}$  and corresponds to going from  $[A]_b$  to  $1/2 [A]_b$ . The second half-life corresponds to going from  $1/2 [A]_b$  to  $1/4 [A]_b$ .

$$\text{First half-life} = \frac{3}{2[A]_b^2} k; \quad \text{second half-life} = \frac{3}{2\left(\frac{1}{2}[A]_b\right)^2} k = \frac{6}{[A]_b^2} k$$

$$\frac{\text{First half-life}}{\text{Second half-life}} = \frac{\frac{3}{2[A]_b^2} k}{\frac{6}{[A]_b^2} k} = 3/12 = 1/4$$

Because the first half-life is 40. s, the second half-life will be four times this, or 160 s.

103.  $\text{Rate} = k[\text{I}^-][\text{OCl}^-][\text{OH}^-]^2$ ; comparing the first and second experiments:

$$\frac{18.7 \times 10^{-3}}{9.4 \times 10^{-3}} = \frac{k(0.0026)^2(0.012)^2(0.10)^2}{k(0.0013)^2(0.012)^2(0.10)^2}, \quad 2.0 = 2.0^x, \quad x = 1$$

Comparing the first and third experiments:

$$\frac{9.4 \times 10^{-3}}{4.7 \times 10^{-3}} = \frac{k(0.0013)(0.012)^2(0.10)^2}{k(0.0013)(0.0060)^2(0.10)^2}, \quad 2.0 = 2.0^y, \quad y = 1$$

Comparing the first and sixth experiments:

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

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

For the first experiment:

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

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

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

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

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

Amount of A that reacted =  $0.0100 - 0.00690 = 0.0031 M$ .

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

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

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

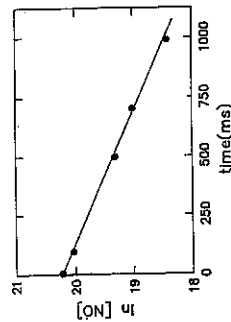
$$\frac{1}{[B]} = k_1 t + \frac{1}{[B]_0}, \quad \frac{1}{2.30 \times 10^{-3} M} = k_2 (180. s) + \frac{1}{2.50 \times 10^{-2} M}$$

$$k_2 = 2.19 \text{ L/mol}\cdot\text{s}$$

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

105. a. We check for first-order dependence by graphing  $\ln[\text{concentration}]$  versus time for each set of data. The rate dependence on NO is determined from the first set of data because the ozone concentration is relatively large compared to the NO concentration, so  $[\text{O}_3]$  is effectively constant.

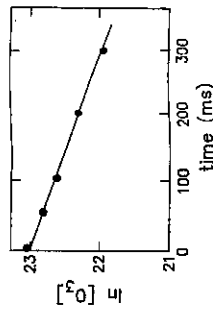
Time (ms)	$[\text{NO}]$ (molecules/cm <sup>3</sup> )	$\ln[\text{NO}]$
0	$6.0 \times 10^8$	20.21
100.	$5.0 \times 10^8$	20.03
500.	$2.4 \times 10^8$	19.30
700.	$1.7 \times 10^8$	18.95
1000.	$9.9 \times 10^7$	18.41



Because  $\ln[\text{NO}]$  versus  $t$  is linear, the reaction is first order with respect to NO.

We follow the same procedure for ozone using the second set of data. The data and plot are:

Time (ms)	$[\text{O}_3]$ (molecules/cm <sup>3</sup> )	$\ln[\text{O}_3]$
0	$1.0 \times 10^{10}$	23.03
50.	$8.4 \times 10^9$	22.85
100.	$7.0 \times 10^9$	22.67
200.	$4.9 \times 10^9$	22.31
300.	$3.4 \times 10^9$	21.95



The plot of  $\ln[\text{O}_3]$  versus  $t$  is linear. Hence the reaction is first order with respect to ozone.

- b. Rate =  $k[\text{NO}][\text{O}_3]$  is the overall rate law.  
 c. For NO experiment, Rate =  $k'[\text{NO}]$  and  $k' = -$  (slope from graph of  $\ln[\text{NO}]$  versus  $t$ ).

$$k' = -\text{slope} = -\frac{18.41 - 20.21}{(1000. - 0) \times 10^{-3} \text{ s}} = 1.8 \text{ s}^{-1}$$

For ozone experiment, Rate =  $k''[\text{O}_3]$  and  $k'' = -$  (slope from  $\ln[\text{O}_3]$  versus  $t$  plot).

$$k'' = -\text{slope} = -\frac{(21.95 - 23.03)}{(300. - 0) \times 10^{-3} \text{ s}} = 3.6 \text{ s}^{-1}$$

- d. From the NO experiment, Rate =  $k[\text{NO}][\text{O}_3] = k'[\text{NO}]$  where  $k' = k[\text{O}_3]$ .

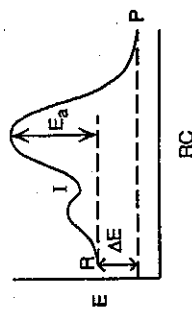
$$k' = 1.8 \text{ s}^{-1} = k(1.0 \times 10^{14} \text{ molecules/cm}^3), \quad k = 1.8 \times 10^{-14} \text{ cm}^3/\text{molecules}\cdot\text{s}$$

We can check this from the ozone data. Rate =  $k''[\text{O}_3] = k[\text{NO}][\text{O}_3]$ , where  $k'' = k[\text{NO}]$ .

$$k'' = 3.6 \text{ s}^{-1} = k(2.0 \times 10^{14} \text{ molecules/cm}^3), \quad k = 1.8 \times 10^{-14} \text{ cm}^3/\text{molecules}\cdot\text{s}$$

Both values of  $k$  agree.

106. On the energy profile to the right, R = reactants, P = products,  $E_a$  = activation energy,  $\Delta E$  = overall energy change for the reaction, I = intermediate, and RC = reaction coordinate, which is the same as reaction progress.



- a-d. See plot to the right.



- c. 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).

$$107. \quad \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right); \text{ assuming } \frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2}{k_1} = 40.0:$$

$$\ln(40.0) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{308 \text{ K}} - \frac{1}{328 \text{ K}} \right), \quad E_a = 1.55 \times 10^5 \text{ J/mol} = 155 \text{ kJ/mol}$$

(carrying an extra sig. fig.)

Note that the activation energy is close to the  $F_2$  bond energy. Therefore, the rate-determining step probably involves breaking the  $F_2$  bond.

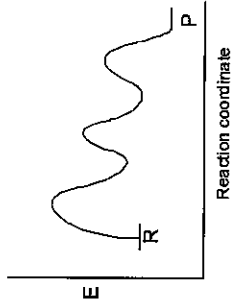
$H_2(g) + F_2(g) \rightarrow 2 HF(g)$ ; for every 2 moles of HF produced, only 1 mole of the reactant is used up. Therefore, to convert the data to  $P_{\text{reactant}}$  versus time,  $P_{\text{reactant}} = 1.00 \text{ atm} - (1/2)P_{\text{HF}}$ .

$P_{\text{reactant}}$	Time
1.000 atm	0 min
0.850 atm	30.0 min
0.700 atm	65.8 min
0.550 atm	110.4 min
0.400 atm	169.1 min
0.250 atm	253.9 min

The plot of  $\ln P_{\text{reactant}}$  versus time (plot not included) is linear with negative slope, so the reaction is first order with respect to the limiting reagent.

For the reactant in excess, because the values of the rate constant are the same for both experiments, one can conclude that the reaction is zero order in the excess reactant.

- a. For a three-step reaction with the first step limiting, the energy-level diagram could be:



Note that the heights of the second and third humps must be lower than the first-step activation energy. However, the height of the third hump could be higher than the second hump. One cannot determine this absolutely from the information in the problem.

- b. We know the reaction has a slow first step, and the calculated activation energy indicates that the rate-determining step involves breaking the  $F_2$  bond. The reaction is also first order in one of the reactants and zero order in the other reactant. All this points to  $F_2$  being the limiting reagent. The reaction is first order in  $F_2$ , and the rate-determining step in the mechanism is  $F_2 \rightarrow 2 F$ . Possible second and third steps to complete the mechanism follow.



- c.  $F_2$  was the limiting reactant.

$$108. \quad \text{We need the value of } k \text{ at } 500. \text{ K}; \quad \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left( \frac{k_2}{2.3 \times 10^{-12} \text{ L/mol} \cdot \text{s}} \right) = \frac{1.11 \times 10^5 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{273 \text{ K}} - \frac{1}{500 \text{ K}} \right) = 22.2$$

$$\frac{k_2}{2.3 \times 10^{-12}} = e^{22.2}, \quad k_2 = 1.0 \times 10^{-2} \text{ L/mol} \cdot \text{s}$$

Because the decomposition reaction is an elementary reaction, the rate law can be written using the coefficients in the balanced equation. For this reaction,  $\text{Rate} = k[\text{NO}_2]^2$ . To solve for the time, we must use the integrated rate law for second-order kinetics. The major problem now is converting units so they match. Rearranging the ideal gas law gives  $n/V = P/RT$ . Substituting  $P/RT$  for concentration units in the second-order integrated rate equation:

$$\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}, \quad \frac{1}{P_0/RT} - \frac{1}{P_0} = \frac{RT}{P_0} \left( \frac{P_0 - P}{P \times P_0} \right)$$

$$t = \frac{(0.08206 \text{ L atm/K} \cdot \text{mol})(500. \text{ K})}{1.0 \times 10^{-2} \text{ L/mol} \cdot \text{s}} \times \left( \frac{2.5 \text{ atm} - 1.5 \text{ atm}}{1.5 \text{ atm} \times 2.5 \text{ atm}} \right) = 1.1 \times 10^3 \text{ s}$$

109. a.  $[\text{B}] \gg [\text{A}]$ , so  $[\text{B}]$  can be considered constant over the experiments. This gives us a pseudo-order rate law equation.

b. Note that in each case, the half-life doubles as times increases (in experiment 1, the first half-life is 40. s, and the second half-life is 80. s; in experiment 2, the first half-life is 20. s, and the second half-life is 40. s). This occurs only for a second-order reaction, so the reaction is second order in  $[\text{A}]$ . Between experiment 1 and experiment 2, we double  $[\text{B}]$ , and the reaction rate doubles, thus it is first order in  $[\text{B}]$ . The overall rate law equation is  $\text{rate} = k[\text{A}]^2[\text{B}]$ .

$$\text{Using } t_{1/2} = \frac{1}{k[\text{A}]_0}, \text{ we get } k = \frac{1}{(40. \text{ s})(10.0 \times 10^{-2} \text{ mol/L})} = 0.25 \text{ L/mol} \cdot \text{s}, \text{ but this is actually } k', \text{ where } \text{Rate} = k'[\text{A}]^2 \text{ and } k' = k[\text{B}].$$

$$k = \frac{k'}{[\text{B}]} = \frac{0.25 \text{ L/mol} \cdot \text{s}}{5.0 \text{ mol/L}} = 0.050 \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

110. a.  $\text{Rate} = k[\text{A}]^2[\text{B}]$ ; looking at the data in experiment 2, notice that the concentration of A is cut in half every 10. s. Only first-order reactions have a half-life that is independent of concentration. The reaction is first order in A. In the data for experiment 1, notice that the half-life is 40. s. This indicates that in going from experiment 1 to experiment 2, where the B concentration doubled, the rate of reaction increased by a factor of four. This tells us that the reaction is second order in B.

$$\text{Rate} = k[\text{A}]^2[\text{B}]^2$$

b. This reaction in each experiment is pseudo-first order in  $[\text{A}]$  because the concentration of B is so large, it is basically constant.

$$\text{Rate} = k[\text{B}]^2[\text{A}] = k'[\text{A}], \text{ where } k' = k[\text{B}]^2$$

For a first-order reaction, the integrated rate law is:

$$\ln \left( \frac{[\text{A}]}{[\text{A}]_0} \right) = -k't$$

Use any set of data you want to calculate  $k$ . For example, in experiment 1, from 0 to 20. s the concentration of A decreased from 0.010 M to 0.0071 M:

$$\ln \left( \frac{0.0071}{0.010} \right) = -k'(20. \text{ s}), \quad k' = 1.7 \times 10^{-2} \text{ s}^{-1}$$

$$k' = k[\text{B}]^2, \quad 1.7 \times 10^{-2} \text{ s}^{-1} = k(10.0 \text{ mol/L})^2$$

$$k = 1.7 \times 10^{-4} \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

We get similar values for  $k$  using other data from either experiment 1 or experiment 2.

$$\text{c. } \ln \left( \frac{[\text{A}]}{0.010 \text{ M}} \right) = -k't = -(1.7 \times 10^{-2} \text{ L}^2/\text{mol}^2 \cdot \text{s}) \times 30. \text{ s}, \quad [\text{A}] = 6.0 \times 10^{-3} \text{ M}$$

111.  $\text{Rate} = k[\text{A}]^2[\text{B}][\text{C}]^2$ ; during the course of experiment 1,  $[\text{A}]$  and  $[\text{C}]$  are essentially constant, and  $\text{Rate} = k'[\text{B}]$ , where  $k' = k[\text{A}]_0^2[\text{C}]_0^2$ .

$[\text{B}]$ (M)	Time (s)	$\ln[\text{B}]$	$1/[\text{B}]$ ( $\text{M}^{-1}$ )
$1.0 \times 10^{-3}$	0	-6.91	$1.0 \times 10^3$
$2.7 \times 10^{-4}$	$1.0 \times 10^5$	-8.22	$3.7 \times 10^3$
$1.6 \times 10^{-4}$	$2.0 \times 10^5$	-8.74	$6.3 \times 10^3$
$1.1 \times 10^{-4}$	$3.0 \times 10^5$	-9.12	$9.1 \times 10^3$
$8.5 \times 10^{-5}$	$4.0 \times 10^5$	-9.37	$12 \times 10^3$
$6.9 \times 10^{-5}$	$5.0 \times 10^5$	-9.58	$14 \times 10^3$
$5.8 \times 10^{-5}$	$6.0 \times 10^5$	-9.76	$17 \times 10^3$

A plot of  $1/[\text{B}]$  versus  $t$  is linear (plot not included), so the reaction is second order in B, and the integrated rate equation is:

$$1/[\text{B}] = (2.7 \times 10^{-2} \text{ L/mol} \cdot \text{s})t + 1.0 \times 10^3 \text{ L/mol}, \quad k' = 2.7 \times 10^{-2} \text{ L/mol} \cdot \text{s}$$

For experiment 2,  $[\text{B}]$  and  $[\text{C}]$  are essentially constant, and  $\text{Rate} = k''[\text{A}]^2$ , where  $k'' = k[\text{B}]_0^2[\text{C}]_0^2$ .

$[\text{A}]$ (M)	Time (s)	$\ln[\text{A}]$	$1/[\text{A}]$ ( $\text{M}^{-1}$ )
$1.0 \times 10^{-2}$	0	-4.61	$1.0 \times 10^2$
$8.9 \times 10^{-3}$	1.0	-4.95	140
$5.5 \times 10^{-3}$	5.0	-5.20	180
$3.8 \times 10^{-3}$	8.0	-5.57	260
$2.9 \times 10^{-3}$	10.0	-5.84	340
$2.0 \times 10^{-3}$	13.0	-6.21	$5.0 \times 10^2$

A plot of  $\ln[\text{A}]$  versus  $t$  is linear, so the reaction is first order in A, and the integrated rate law is:

$$\ln[\text{A}] = -(0.123 \text{ s}^{-1})t - 4.61; \quad k'' = 0.123 \text{ s}^{-1}$$

Note: We will carry an extra significant figure in  $k''$ .

Experiment 3:  $[A]$  and  $[B]$  are constant. Rate =  $k''[C]^z$

The plot of  $[C]$  versus  $t$  is linear. Thus  $z = 0$ .

The overall rate law is Rate =  $k[A][B]^2$ .

From Experiment 1 (to determine  $k$ ):

$$k' = 2.7 \times 10^{-2} \text{ L/mol}\cdot\text{s} = k[A]_0^2[C]_0^2 = k[A]_0^2 = k(2.0 \text{ M}), \quad k = 1.4 \times 10^{-2} \text{ L}^2/\text{mol}^2\cdot\text{s}$$

$$\text{From Experiment 2: } k'' = 0.123 \text{ s}^{-1} = k[B]_0^2 = k(3.0 \text{ M})^2 = 1.4 \times 10^{-2} \text{ L}^2/\text{mol}^2\cdot\text{s}$$

Thus Rate =  $k[A][B]^2$  and  $k = 1.4 \times 10^{-2} \text{ L}^2/\text{mol}^2\cdot\text{s}$ .

$$112. \quad \text{a. Rate} = (k_1 + k_2[H^+])[I^-][H_2O_2]^m$$

In all the experiments, the concentration of  $H_2O_2$  is small compared to the concentrations of  $I^-$  and  $H^+$ . Therefore, the concentrations of  $I^-$  and  $H^+$  are effectively constant, and the rate law reduces to:

$$\text{Rate} = k_{\text{obs}}[H_2O_2]^m, \quad \text{where } k_{\text{obs}} = (k_1 + k_2[H^+])[I^-]^m$$

Because all plots of  $\ln[H_2O_2]$  versus time are linear, the reaction is first order with respect to  $H_2O_2$  ( $n = 1$ ). The slopes of the  $\ln[H_2O_2]$  versus time plots equal  $-k_{\text{obs}}$ , which equals  $-(k_1 + k_2[H^+])[I^-]^m$ . To determine the order of  $I^-$ , compare the slopes of two experiments in which  $I^-$  changes and  $H^+$  is constant. Comparing the first two experiments:

$$\text{slope (exp. 2)} = -0.360 = -(k_1 + k_2(0.0400 \text{ M}))(0.3000 \text{ M})^m$$

$$\text{slope (exp. 1)} = -0.120 = -(k_1 + k_2(0.0400 \text{ M}))(0.1000 \text{ M})^m$$

$$3.00 = \left( \frac{0.3000 \text{ M}}{0.1000 \text{ M}} \right)^m = (3.000)^m, \quad m = 1$$

The reaction is also first order with respect to  $I^-$ .

b. The slope equation has two unknowns,  $k_1$  and  $k_2$ . To solve for  $k_1$  and  $k_2$ , we must have two equations. We need to take one of the first set of three experiments and one of the second set of three experiments to generate the two equations in  $k_1$  and  $k_2$ .

Experiment 1: Slope =  $-(k_1 + k_2[H^+])[I^-]$

$$-0.120 \text{ min}^{-1} = -(k_1 + k_2(0.0400 \text{ M}))(0.1000 \text{ M}) \text{ or } 1.20 = k_1 + k_2(0.0400)$$

Experiment 4:

$$-0.0760 \text{ min}^{-1} = -(k_1 + k_2(0.0200 \text{ M}))(0.0750 \text{ M}) \text{ or } 1.01 = k_1 + k_2(0.0200)$$

Subtracting 4 from 1:

$$1.20 = k_1 + k_2(0.0400)$$

$$-1.01 = -k_1 - k_2(0.0200)$$

$$0.19 = k_2(0.0200), \quad k_2 = 9.5 \text{ L}^2/\text{mol}^2\cdot\text{min}$$

$$1.20 = k_1 + 9.5(0.0400), \quad k_1 = 0.82 \text{ L/mol}\cdot\text{min}$$

c. There are two pathways, one involving  $H^+$  with Rate =  $k_2[H^+][H_2O_2]$  and another not involving  $H^+$  with Rate =  $k_1[H_2O_2]$ . The overall rate of reaction depends on which of these two pathways dominates, and this depends on the  $H^+$  concentration.

### Integrative Problems

$$113. \quad 8.75 \text{ h} \times \frac{3600 \text{ s}}{\text{h}} = 3.15 \times 10^4 \text{ s}; \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{3.15 \times 10^4 \text{ s}} = 2.20 \times 10^{-5} \text{ s}^{-1}$$

The partial pressure of a gas is directly related to the concentration in mol/L. So, instead of using mol/L as the concentration units in the integrated first-order rate law, we can use partial pressures of  $SO_2Cl_2$ .

$$\ln\left(\frac{P}{P_0}\right) = -kt, \quad \ln\left(\frac{P}{791 \text{ torr}}\right) = -(2.20 \times 10^{-5} \text{ s}^{-1}) \times 12.5 \text{ h} \times \frac{3600 \text{ s}}{\text{h}}$$

$$P_{SO_2Cl_2} = 294 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.387 \text{ atm}$$

$$n = \frac{PV}{RT} = \frac{0.387 \text{ atm} \times 1.25 \text{ L}}{0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 593 \text{ K}} = 9.94 \times 10^{-3} \text{ mol } SO_2Cl_2$$

$$9.94 \times 10^{-3} \text{ mol} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = 5.99 \times 10^{21} \text{ molecules } SO_2Cl_2$$

$$114. \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{667 \text{ s}} = 1.04 \times 10^{-3} \text{ s}^{-1}$$

$$[\text{In}^+]_0 = \frac{2.38 \text{ g InCl} \times \frac{1 \text{ mol InCl}}{150.3 \text{ g}} \times \frac{1 \text{ mol In}^+}{\text{mol InCl}}}{0.500 \text{ L}} = 0.0317 \text{ mol/L}$$

$$\ln\left(\frac{[\text{In}^+]}{[\text{In}^+]_0}\right) = -kt, \quad \ln\left(\frac{[\text{In}^+]}{0.0317 \text{ M}}\right) = -(1.04 \times 10^{-3} \text{ s}^{-1}) \times 1.25 \text{ h} \times \frac{3600 \text{ s}}{\text{h}}$$

$$[\text{In}^+] = 2.94 \times 10^{-4} \text{ mol/L}$$

The balanced equation for the reaction is:  $3 \text{In}^+(\text{aq}) \rightarrow 2 \text{In}(s) + \text{In}^{3+}(\text{aq})$

$$\text{Mol In}^+ \text{ reacted} = 0.500 \text{ L} \times \frac{0.0317 \text{ mol}}{\text{L}} - 0.500 \text{ L} \times \frac{2.94 \times 10^{-4} \text{ mol}}{\text{L}} = 1.57 \times 10^{-2} \text{ mol In}^+$$

$$1.57 \times 10^{-2} \text{ mol In}^+ \times \frac{2 \text{ mol In}}{3 \text{ mol In}^+} \times \frac{114.8 \text{ g In}}{\text{mol In}} = 1.20 \text{ g In}$$

$$115. \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right); \ln\left(\frac{1.7 \times 10^{-2} \text{ s}^{-1}}{7.2 \times 10^{-4} \text{ s}^{-1}}\right) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{660. \text{ K}} - \frac{1}{720. \text{ K}} \right)$$

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

For  $k$  at  $325^\circ\text{C}$  ( $598 \text{ K}$ ):

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

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.

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

### Marathon Problem

116. a.  $\text{Rate} = k[\text{CH}_3\text{X}][\text{Y}]^y$ ; for experiment 1,  $[\text{Y}]$  is in large excess, so its concentration will be constant.  $\text{Rate} = k'[\text{CH}_3\text{X}]^x$ , where  $k' = k(3.0 \text{ M})^y$ .

A plot (not included) of  $\ln[\text{CH}_3\text{X}]$  versus  $t$  is linear ( $x = 1$ ). The integrated rate law is:

$$\ln[\text{CH}_3\text{X}] = -(0.93)t - 3.99, k' = 0.93 \text{ h}^{-1}$$

For experiment 2,  $[\text{Y}]$  is again constant, with  $\text{Rate} = k''[\text{CH}_3\text{X}]^x$ , where  $k'' = k(4.5 \text{ M})^y$ . The natural log plot is linear again with an integrated rate law:

$$\ln[\text{CH}_3\text{X}] = -(0.93)t - 5.40; k'' = 0.93 \text{ h}^{-1}$$

$$\text{Dividing the rate-constant values: } \frac{k'}{k''} = \frac{0.93}{0.93} = \frac{k(3.0)^y}{k(4.5)^y}, 1.0 = (0.67)^y, y = 0$$

The reaction is first order in  $\text{CH}_3\text{X}$  and zero order in  $\text{Y}$ . The overall rate law is:

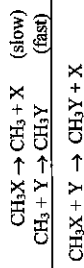
$$\text{Rate} = k[\text{CH}_3\text{X}], \text{ where } k = 0.93 \text{ h}^{-1} \text{ at } 25^\circ\text{C}$$

$$\text{b. } t_{1/2} = (\ln 2)/k = 0.6931/(7.88 \times 10^8 \text{ h}^{-1}) = 8.80 \times 10^{-10} \text{ hour}$$

$$\text{c. } \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right), \ln\left(\frac{7.88 \times 10^8}{0.93}\right) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{298 \text{ K}} - \frac{1}{358 \text{ K}} \right)$$

$$E_a = 3.0 \times 10^5 \text{ J/mol} = 3.0 \times 10^2 \text{ kJ/mol}$$

d. From part a, the reaction is first order in  $\text{CH}_3\text{X}$  and zero order in  $\text{Y}$ . From part c, the activation energy is close to the C-X bond energy. A plausible mechanism that explains the results in parts a and c is:



Note: This is a plausible mechanism because the derived rate law is the same as the experimental rate law (and the sum of the steps gives the overall balanced equation).