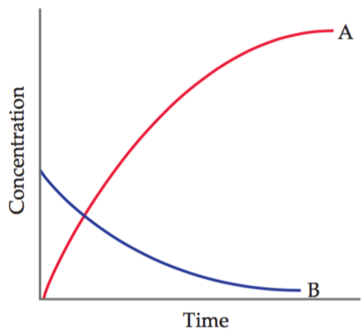
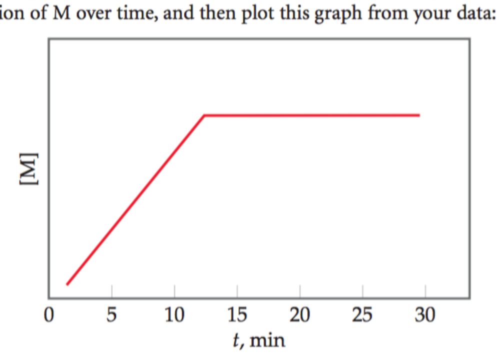
Chemical Kinetics and Reaction Mechanisms Problem Set

14.3 You study the rate of a reaction, measuring both the concentration of the reactant and the concentration of the product as a function of time, and obtain the following results:



Which chemical equation is consistent with these data: **(a)** $A \longrightarrow B$, **(b)** $B \longrightarrow A$, **(c)** $A \longrightarrow 2\,B$, **(d)** $B \longrightarrow 2\,A$? Explain your choice. [Section 14.2]

14.4 You perform the reaction $K + L \rightarrow M$, monitor the production of M over time, and then plot this graph from your data:

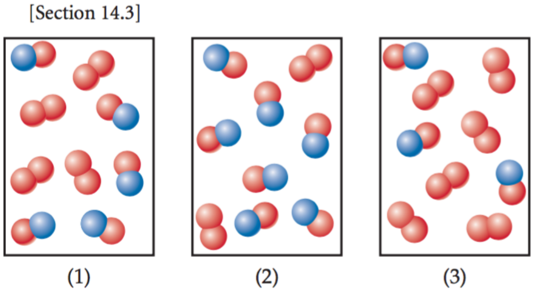


(a) Is the reaction occurring at a constant rate from $t = 0$ to $t = 15$ min? Explain. **(b)** Is the reaction completed at $t = 15$ min? Explain.

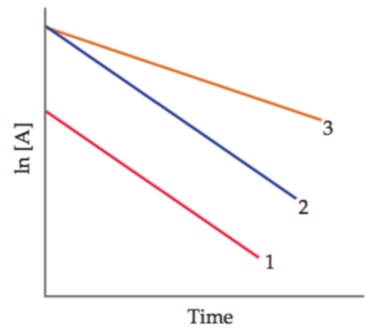
14.6 The following diagrams represent mixtures of $NO(g)$ and $O_2(g)$. These two substances react as follows:

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

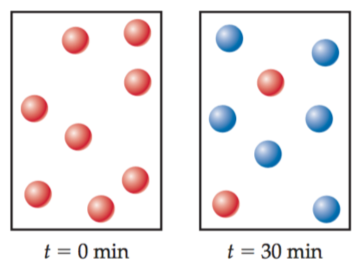
It has been determined experimentally that the rate is second order in NO and first order in O_2. Based on this fact, which of the following mixtures will have the fastest initial rate? [Section 14.3]



14.7 A friend studies a first-order reaction and obtains the following three graphs for experiments done at two different temperatures. **(a)** Which two graphs represent experiments done at the same temperature? What accounts for the difference in these two graphs? In what way are they the same? **(b)** Which two graphs represent experiments done with the same starting concentration but at different temperatures? Which graph probably represents the lower temperature? How do you know? [Section 14.4]



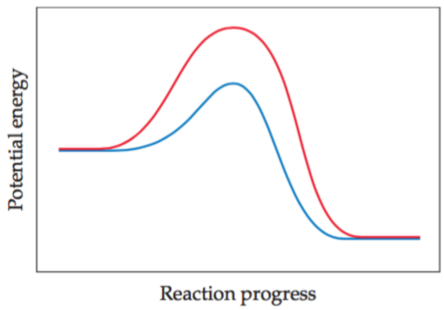
14.8 **(a)** Given the following diagrams at $t = 0$ min and $t = 30$ min, what is the half-life of the reaction if it follows first-order kinetics?



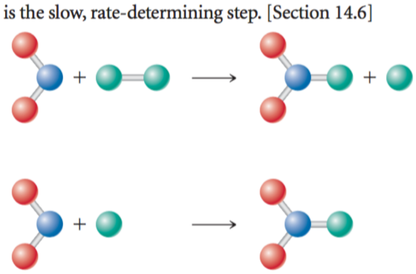
(b) After four half-life periods for a first-order reaction, what fraction of reactant remains? [Section 14.4]

14.10 You study the effect of temperature on the rate of two reactions and graph the natural logarithm of the rate constant for each reaction as a function of $1/T$. How do the two graphs compare **(a)** if the activation energy of the second reaction is higher than the activation energy of the first reaction but the two reactions have the same frequency factor, and **(b)** if the frequency factor of the second reaction is higher than the frequency factor of the first reaction but the two reactions have the same activation energy? [Section 14.5]

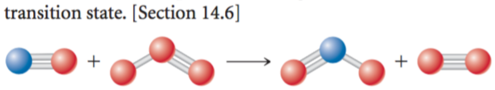
14.11 The following graph shows two different reaction pathways for the same overall reaction at the same temperature. (a) Which pathway is slower? Why? (b) How can there be two different reaction pathways for the same reaction at the same temperature? Discuss. [Section 14.6]



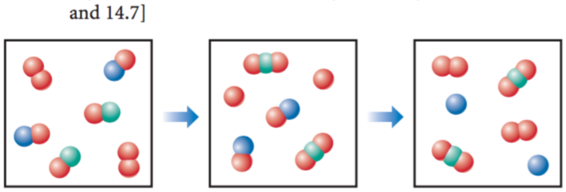
14.12 Consider the diagram that follows, which represents two steps in an overall reaction. The red spheres are oxygen, the blue ones nitrogen, and the green ones fluorine. **(a)** Write the chemical equation for each step in the reaction. **(b)** Write the equation for the overall reaction. **(c)** Identify the intermediate in the mechanism. **(d)** Write the rate law for the overall reaction if the first step is the slow, rate-determining step. [Section 14.6]



14.14 Draw a possible transition state for the bimolecular reaction depicted here. (The blue spheres are nitrogen atoms, and the red ones are oxygen atoms.) Use dashed lines to represent the bonds that are in the process of being broken or made in the transition state. [Section 14.6]



14.15 The following diagram represents an imaginary two-step mechanism. Let the red spheres represent element A, the green ones element B, and the blue ones element C. **(a)** Write the equation for the net reaction that is occurring. **(b)** Identify the intermediate. **(c)** Identify the catalyst. [Sections 14.6 and 14.7]



14.20 A flask is charged with 0.100 mol of A and allowed to react to form B according to the hypothetical gas-phase reaction $A(g) \longrightarrow B(g)$. The following data are collected:

Time (s)	0	40	80	120	160
Moles of A	0.100	0.067	0.045	0.030	0.020

(a) Calculate the number of moles of B at each time in the table, assuming that A is cleanly converted to B with no intermediates. **(b)** Calculate the average rate of disappearance of A for each 40-s interval in units of mol/s. **(c)** What additional information would be needed to calculate the rate in units of concentration per time?

14.21 The isomerization of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) was studied in the gas phase at 215 °C, and the following data were obtained:

Time (s)	$[CH_3NC]$ (M)
0	0.0165
2,000	0.0110
5,000	0.00591
8,000	0.00314
12,000	0.00137
15,000	0.00074

(a) Calculate the average rate of reaction, in M/s, for the time interval between each measurement. **(b)** Calculate the average rate of reaction over the entire time of the data from $t = 0$ to $t = 15{,}000$ s. **(c)** Graph $[CH_3NC]$ versus time and determine the instantaneous rates in M/s at $t = 5000$ s and $t = 8000$ s.

14.23 For each of the following gas-phase reactions, indicate how the rate of disappearance of each reactant is related to the rate of appearance of each product:

(a) $H_2O_2(g) \longrightarrow H_2(g) + O_2(g)$

(b) $2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$

(c) $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$

(d) $C_2H_5NH_2(g) \longrightarrow C_2H_4(g) + NH_3(g)$

14.24 For each of the following gas-phase reactions, write the rate expression in terms of the appearance of each product and disappearance of each reactant:

(a) $2\,H_2O(g) \longrightarrow 2\,H_2(g) + O_2(g)$

(b) $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

(c) $2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$

(d) $N_2(g) + 2\,H_2(g) \longrightarrow N_2H_4(g)$

14.25 **(a)** Consider the combustion of $H_2(g)$: $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$. If hydrogen is burning at the rate of 0.48 mol/s, what is the rate of consumption of oxygen? What is the rate of formation of water vapor? **(b)** The reaction $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$ is carried out in a closed vessel. If the partial pressure of NO is decreasing at the rate of 56 torr/min, what is the rate of change of the total pressure of the vessel?

14.28 Consider a hypothetical reaction between A, B, and C that is first order in A, zero order in B, and second order in C. **(a)** Write the rate law for the reaction. **(b)** How does the rate change when [A] is doubled and the other reactant concentrations are held constant? **(c)** How does the rate change when [B] is tripled and the other reactant concentrations are held constant? **(d)** How does the rate change when [C] is tripled and the other reactant concentrations are held constant? **(e)** By what factor does the rate change when the concentrations of all three reactants are tripled? **(f)** By what factor does the rate change when the concentrations of all three reactants are cut in half?

14.31 Consider the following reaction:

$$CH_3Br(aq) + OH^-(aq) \longrightarrow CH_3OH(aq) + Br^-(aq)$$

The rate law for this reaction is first order in CH_3Br and first order in OH^-. When $[CH_3Br]$ is 5.0×10^{-3} *M* and $[OH^-]$ is 0.050 *M*, the reaction rate at 298 K is 0.0432 *M*/s. **(a)** What is the value of the rate constant? **(b)** What are the units of the rate constant? **(c)** What would happen to the rate if the concentration of OH^- were tripled? (d) What would happen to the rate if the concentration of both reactants were tripled?

14.32 The reaction between ethyl bromide (C_2H_5Br) and hydroxide ion in ethyl alcohol at 330 K, $C_2H_5Br(alc) + OH^-(alc) \longrightarrow C_2H_5OH(l) + Br^-(alc)$, is first order each in ethyl bromide and hydroxide ion. When $[C_2H_5Br]$ is 0.0477 *M* and $[OH^-]$ is 0.100 *M*, the rate of disappearance of ethyl bromide is 1.7×10^{-7} *M*/s. **(a)** What is the value of the rate constant? **(b)** What are the units of the rate constant? **(c)** How would the rate of disappearance of ethyl bromide change if the solution were diluted by adding an equal volume of pure ethyl alcohol to the solution?

[14.37] Consider the gas-phase reaction between nitric oxide and bromine at 273 °C: $2\,NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g)$. The following data for the initial rate of appearance of NOBr were obtained:

Experiment	[NO] (*M*)	$[Br_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

(a) Determine the rate law. **(b)** Calculate the average value of the rate constant for the appearance of NOBr from the four data sets. **(c)** How is the rate of appearance of NOBr related to the rate of disappearance of Br_2? **(d)** What is the rate of disappearance of Br_2 when [NO] = 0.075 *M* and $[Br_2]$ = 0.25 *M*?

[14.38] Consider the reaction of peroxydisulfate ion ($S_2O_8^{2-}$) with iodide ion (I^-) in aqueous solution:

14.44 Molecular iodine, $I_2(g)$, dissociates into iodine atoms at 625 K with a first-order rate constant of $0.271\ s^{-1}$. **(a)** What is the half-life for this reaction? **(b)** If you start with 0.050 *M* I_2 at this temperature, how much will remain after 5.12 s assuming that the iodine atoms do not recombine to form I_2?

Experiment	$[S_2O_8^{2-}]$ (*M*)	$[I^-]$ (*M*)	Initial Rate (*M*/s)
1	0.018	0.036	2.6×10^{-6}
2	0.027	0.036	3.9×10^{-6}
3	0.036	0.054	7.8×10^{-6}
4	0.050	0.072	1.4×10^{-5}

(a) Determine the rate law for the reaction and state the units of the rate constant. **(b)** What is the average value of the rate constant for the disappearance of $S_2O_8^{2-}$ based on the four sets of data? **(c)** How is the rate of disappearance of $S_2O_8^{2-}$ related to the rate of disappearance of I^-? **(d)** What is the rate of disappearance of I^- when $[S_2O_8^{2-}]$ = 0.025 *M* and $[I^-]$ = 0.050 *M*?

14.41 For the generic reaction A $\longrightarrow$ B that is zero order in A, what would you graph in order to obtain the rate constant?

14.42 Sketch a graph for the generic first-order reaction A $\longrightarrow$ B that has concentration of A on the vertical axis and time on the horizontal axis. (a) Is this graph linear? Explain. (b) Indicate on your graph the half-life for the reaction.

14.47 The reaction

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

is first order in SO_2Cl_2. Using the following kinetic data, determine the magnitude and units of the first-order rate constant:

Time (s)	Pressure SO_2Cl_2 (atm)
0	1.000
2,500	0.947
5,000	0.895
7,500	0.848
10,000	0.803

14.43 **(a)** The gas-phase decomposition of SO_2Cl_2, $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$, is first order in SO_2Cl_2. At 600 K the half-life for this process is 2.3×10^5 s. What is the rate constant at this temperature? **(b)** At 320 °C the rate constant is $2.2 \times 10^{-5}\ s^{-1}$. What is the half-life at this temperature?

14.52 Sucrose ($C_{12}H_{22}O_{11}$), commonly known as table sugar, reacts in dilute acid solutions to form two simpler sugars, glucose and fructose, both of which have the formula $C_6H_{12}O_6$. At 23 °C and in 0.5 *M* HCl, the following data were obtained for the disappearance of sucrose:

Time (min)	$[C_{12}H_{22}O_{11}]$ (*M*)
0	0.316
39	0.274
80	0.238
140	0.190
210	0.146

(a) Is the reaction first order or second order with respect to $[C_{12}H_{22}O_{11}]$? **(b)** What is the rate constant? **(c)** Using this rate constant, calculate the concentration of sucrose at 39, 80, 140, and 210 min if the initial sucrose concentration was 0.316 *M* and the reaction was zero order in sucrose.

14.53 **(a)** What factors determine whether a collision between two molecules will lead to a chemical reaction? **(b)** According to the collision model, why does temperature affect the value of the rate constant? **(c)** Does the rate constant for a reaction generally increase or decrease with an increase in reaction temperature?

14.54 **(a)** In which of the following reactions would you expect the orientation factor to be least important in leading to reaction: $NO + O \longrightarrow NO_2$ or $H + Cl \longrightarrow HCl$? **(b)** How does the kinetic-molecular theory help us understand the temperature dependence of chemical reactions?

14.57 The gas-phase reaction $Cl(g) + HBr(g) \longrightarrow HCl(g) + Br(g)$ has an overall enthalpy change of −66 kJ. The activation energy for the reaction is 7 kJ. **(a)** Sketch the energy profile for the reaction, and label E_a and ΔE. **(b)** What is the activation energy for the reverse reaction?

14.59 Indicate whether each statement is true or false. If it is false, rewrite it so that it is true.
- **(a)** If you compare two reactions with similar collision factors, the one with the larger activation energy will be faster.
- **(b)** A reaction that has a small rate constant must have a small frequency factor.
- **(c)** Increasing the reaction temperature increases the fraction of successful collisions between reactants.

14.60 Indicate whether each statement is true or false. If it is false, rewrite it so that it is true.
- **(a)** If you measure the rate constant for a reaction at different temperatures, you can calculate the overall enthalpy change for the reaction.
- **(b)** Exothermic reactions are faster than endothermic reactions.
- **(c)** If you double the temperature for a reaction, you cut the activation energy in half.

14.61 Based on their activation energies and energy changes and assuming that all collision factors are the same, which of the following reactions would be fastest and which would be slowest? Explain your answer.
- **(a)** $E_a = 45$ kJ/mol; $\Delta E = -25$ kJ/mol
- **(b)** $E_a = 35$ kJ/mol; $\Delta E = -10$ kJ/mol
- **(c)** $E_a = 55$ kJ/mol; $\Delta E = 10$ kJ/mol

14.62 Which of the reactions in Exercise 14.61 will be fastest in the reverse direction? Which will be slowest? Explain.

14.64 Understanding the high-temperature behavior of nitrogen oxides is essential for controlling pollution generated in automobile engines. The decomposition of nitric oxide (NO) to N_2 and O_2 is second order with a rate constant of 0.0796 $M^{-1}\,s^{-1}$ at 737 °C and 0.0815 $M^{-1}\,s^{-1}$ at 947 °C. Calculate the activation energy for the reaction.

14.66 The temperature dependence of the rate constant for a reaction is tabulated as follows:

Temperature (K)	*k* ($M^{-1}\,s^{-1}$)
600	0.028
650	0.22
700	1.3
750	6.0
800	23

Calculate E_a and *A*.

14.69 **(a)** What is meant by the term *elementary reaction*? **(b)** What is the difference between a *unimolecular* and a *bimolecular* elementary reaction? **(c)** What is a *reaction mechanism*?

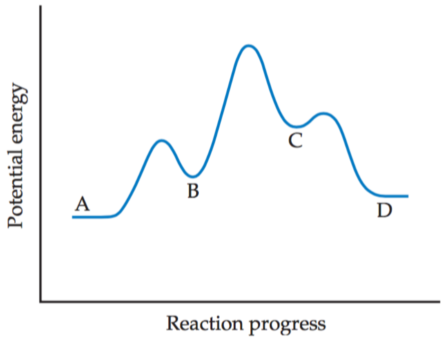
14.70 **(a)** What is meant by the term *molecularity*? **(b)** Why are termolecular elementary reactions so rare? **(c)** What is an *intermediate* in a mechanism?

14.71 What are the differences between an intermediate and a transition state?

14.72 What is meant by the term *rate-determining step*?

14.73 What is the molecularity of each of the following elementary reactions? Write the rate law for each.
- **(a)** $Cl_2(g) \longrightarrow 2\,Cl(g)$
- **(b)** $OCl^-(aq) + H_2O(l) \longrightarrow HOCl(aq) + OH^-(aq)$
- **(c)** $NO(g) + Cl_2(g) \longrightarrow NOCl_2(g)$

14.75 **(a)** Based on the following reaction profile, how many intermediates are formed in the reaction A $\longrightarrow$ D? **(b)** How many transition states are there? **(c)** Which step is the fastest? **(d)** Is the reaction A $\longrightarrow$ D exothermic or endothermic?

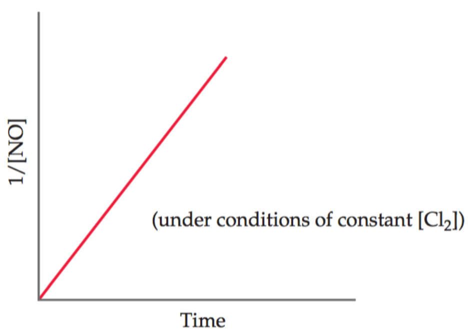


14.78 The decomposition of hydrogen peroxide is catalyzed by iodide ion. The catalyzed reaction is thought to proceed by a two-step mechanism:

$$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(l) + IO^-(aq) \quad \text{(slow)}$$
$$IO^-(aq) + H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g) + I^-(aq) \quad \text{(fast)}$$

(a) Write the chemical equation for the overall process. **(b)** Identify the intermediate, if any, in the mechanism. **(c)** Assuming that the first step of the mechanism is rate determining, predict the rate law for the overall process.

14.79 The reaction $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$ was performed and the following data obtained:



Is the following mechanism consistent with the data? Explain.

$$NO(g) + Cl_2(g) \longrightarrow NOCl_2(g)$$
$$NOCl_2(g) + NO(g) \longrightarrow 2\,NOCl(g)$$

14.80 You have studied the gas-phase oxidation of HBr by O_2:

$$4\,HBr(g) + O_2(g) \longrightarrow 2\,H_2O(g) + 2\,Br_2(g)$$

You find the reaction to be first order with respect to HBr and first order with respect to O_2. You propose the following mechanism:

$$HBr(g) + O_2(g) \longrightarrow HOOBr(g)$$
$$HOOBr(g) + HBr(g) \longrightarrow 2\,HOBr(g)$$
$$HOBr(g) + HBr(g) \longrightarrow H_2O(g) + Br_2(g)$$

(a) Confirm that the elementary reactions add to give the overall reaction. **(b)** Based on the experimentally determined rate law, which step is rate determining? **(c)** What are the intermediates in this mechanism? **(d)** If you are unable to detect HOBr or HOOBr among the products, does this disprove your mechanism?

14.81 **(a)** What is a catalyst? **(b)** What is the difference between a homogeneous and a heterogeneous catalyst? **(c)** Do catalysts affect the overall enthalpy change for a reaction, the activation energy, or both?

14.82 **(a)** Most commercial heterogeneous catalysts are extremely finely divided solid materials. Why is particle size important? **(b)** What role does adsorption play in the action of a heterogeneous catalyst?

14.84 In solution, chemical species as simple as H^+ and OH^- can serve as catalysts for reactions. Imagine you could measure the $[H^+]$ of a solution containing an acid-catalyzed reaction as it occurs. Assume the reactants and products themselves are neither acids nor bases. Sketch the $[H^+]$ concentration profile you would measure as a function of time for the reaction, assuming $t = 0$ is when you add a drop of acid to the reaction.

14.85 The oxidation of SO_2 to SO_3 is catalyzed by NO_2. The reaction proceeds according to:

$$NO_2(g) + SO_2(g) \longrightarrow NO(g) + SO_3(g)$$
$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

(a) Show that the two reactions can be summed to give the overall oxidation of SO_2 by O_2 to give SO_3. **(b)** Why do we consider NO_2 a catalyst and not an intermediate in this reaction? **(c)** Is this an example of homogeneous catalysis or heterogeneous catalysis?

14.86 NO catalyzes the decomposition of N_2O, possibly by the following mechanism:

$$NO(g) + N_2O(g) \longrightarrow N_2(g) + NO_2(g)$$
$$2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g)$$

(a) What is the chemical equation for the overall reaction? Show how the two steps can be added to give the overall equation. **(b)** Why is NO considered a catalyst and not an intermediate? **(c)** If experiments show that during the decomposition of N_2O, NO_2 does not accumulate in measurable quantities, does this rule out the proposed mechanism? If you think not, suggest what might be going on.