a. Which is greater, T_2 or T_1? How can you tell?
b. What does this plot tell us about the temperature of the rate of a chemical reaction? Explain your answer.

13. For the reaction

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

the observed rate law is

$$\text{Rate} = k[NO]^2[O_2]$$

Which of the changes listed below would affect the value of the rate constant k?
a. increasing the partial pressure of oxygen gas
b. changing the temperature
c. using an appropriate catalyst

14. The rate law for a reaction can be determined only from experiment and not from the balanced equation. Two experimental procedures were outlined in Chapter 12. What are these two procedures? Explain how each method is used to determine rate laws.

15. Table 12.2 illustrates how the average rate of a reaction decreases with time. Why does the average rate decrease with time? How does the instantaneous rate of a reaction depend on time? Why are initial rates used by convention?

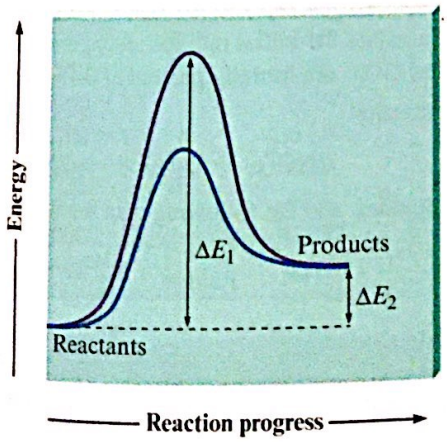
16. The type of rate law for a reaction, either the differential rate law or the integrated rate law, is usually determined by which data is easiest to collect. Explain.

17. The initial rate of a reaction doubles as the concentration of one of the reactants is quadrupled. What is the order of this reactant? If a reactant has a -1 order, what happens to the initial rate when the concentration of that reactant increases by a factor of two?

18. Hydrogen reacts explosively with oxygen. However, a mixture of H_2 and O_2 can exist indefinitely at room temperature. Explain why H_2 and O_2 do not react under these conditions.

19. The central idea of the collision model is that molecules must collide in order to react. Give two reasons why not all collisions of reactant molecules result in product formation.

20. Consider the following energy plots for a chemical reaction when answering the questions below.



a. Which plot (purple or blue) is the catalyzed pathway? How do you know?
b. What does ΔE_1 represent?
c. What does ΔE_2 represent?
d. Is the reaction endothermic or exothermic?

21. Enzymes are kinetically important for many of the complex reactions necessary for plant and animal life to exist. However, only a tiny amount of any particular enzyme is required for these complex reactions to occur. Explain.

22. Would the slope of a $\ln(k)$ versus $1/T$ plot (with temperature in kelvin) for a catalyzed reaction be more or less negative than the slope of the $\ln(k)$ versus $1/T$ plot for the uncatalyzed reaction? Explain. Assume both rate laws are first-order overall.

Exercises

In this section similar exercises are paired.

Reaction Rates

23. Consider the reaction

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

If, in a certain experiment, over a specific time period, 0.0048 mole of PH_3 is consumed in a 2.0-L container each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?

24. In the Haber process for the production of ammonia,

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

what is the relationship between the rate of production of ammonia and the rate of consumption of hydrogen?

25. At 40°C, $H_2O_2(aq)$ will decompose according to the following reaction:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The following data were collected for the concentration of H_2O_2 at various times.

Time (s)	$[H_2O_2]$ (mol/L)
0	1.000
2.16×10^4	0.500
4.32×10^4	0.250

a. Calculate the average rate of decomposition of H_2O_2 between 0 and 2.16×10^4 s. Use this rate to calculate the average rate of production of $O_2(g)$ over the same time period.
b. What are these rates for the time period 2.16×10^4 s to 4.32×10^4 s?

26. Consider the general reaction

$$aA + bB \longrightarrow cC$$

and the following average rate data over some time period Δt:

$$-\frac{\Delta A}{\Delta t} = 0.0080 \text{ mol/L} \cdot \text{s}$$

$$-\frac{\Delta B}{\Delta t} = 0.0120 \text{ mol/L} \cdot \text{s}$$

$$\frac{\Delta C}{\Delta t} = 0.0160 \text{ mol/L} \cdot \text{s}$$

Determine a set of possible coefficients to balance this general reaction.

27. What are the units for each of the following if the concentrations are expressed in moles per liter and the time in seconds?
   a. rate of a chemical reaction
   b. rate constant for a zero-order rate law
   c. rate constant for a first-order rate law
   d. rate constant for a second-order rate law
   e. rate constant for a third-order rate law

28. The rate law for the reaction

$$Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$$

is $\text{Rate} = k[Cl_2]^{1/2}[CHCl_3]$

What are the units for k, assuming time in seconds and concentration in mol/L?

Rate Laws from Experimental Data: Initial Rates Method

29. The reaction

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

was studied at −10°C. The following results were obtained where

$$\text{Rate} = -\frac{\Delta[Cl_2]}{\Delta t}$$

$[NO]_0$ (mol/L)	$[Cl_2]_0$ (mol/L)	Initial Rate (mol/L · min)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

   a. What is the rate law?
   b. What is the value of the rate constant?

30. The reaction

$$2I^-(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

was studied at 25°C. The following results were obtained where

$$\text{Rate} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t}$$

$[I^-]_0$ (mol/L)	$[S_2O_8^{2-}]_0$ (mol/L)	Initial Rate (mol/L · s)
0.080	0.040	12.5×10^{-6}
0.040	0.040	6.25×10^{-6}
0.080	0.020	6.25×10^{-6}
0.032	0.040	5.00×10^{-6}
0.060	0.030	7.00×10^{-6}

   a. Determine the rate law.
   b. Calculate a value for the rate constant for each experiment and an average value for the rate constant.

31. The decomposition of nitrosyl chloride was studied:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

The following data were obtained where

$$\text{Rate} = -\frac{\Delta[NOCl]}{\Delta t}$$

$[NOCl]_0$ (molecules/cm³)	Initial Rate (molecules/cm³ · s)
3.0×10^{16}	5.98×10^{4}
2.0×10^{16}	2.66×10^{4}
1.0×10^{16}	6.64×10^{3}
4.0×10^{16}	1.06×10^{5}

   a. What is the rate law?
   b. Calculate the value of the rate constant.
   c. Calculate the value of the rate constant when concentrations are given in moles per liter.

32. The following data were obtained for the gas-phase decomposition of dinitrogen pentoxide,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$[N_2O_5]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0750	8.90×10^{-4}
0.190	2.26×10^{-3}
0.275	3.26×10^{-3}
0.410	4.85×10^{-3}

Defining the rate as $-\Delta[N_2O_5]/\Delta t$, write the rate law and calculate the value of the rate constant.

33. The reaction

$$I^-(aq) + OCl^-(aq) \longrightarrow IO^-(aq) + Cl^-(aq)$$

was studied, and the following data were obtained:

$[I^-]_0$ (mol/L)	$[OCl^-]_0$ (mol/L)	Initial Rate (mol/L · s)
0.12	0.18	7.91×10^{-2}
0.060	0.18	3.95×10^{-2}
0.030	0.090	9.88×10^{-3}
0.24	0.090	7.91×10^{-2}

   a. What is the rate law?
   b. Calculate the value of the rate constant.
   c. Calculate the initial rate for an experiment where both I^- and OCl^- are initially present at 0.15 mol/L.

34. The reaction

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

was studied, and the following data were obtained where

$$\text{Rate} = -\frac{\Delta[O_2]}{\Delta t}$$

$[NO]_0$ (molecules/cm³)	$[O_2]_0$ (molecules/cm³)	Initial Rate (molecules/cm³ · s)
1.00×10^{18}	1.00×10^{18}	2.00×10^{16}
3.00×10^{18}	1.00×10^{18}	1.80×10^{17}
2.50×10^{18}	2.50×10^{18}	3.13×10^{17}

35. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C. The following data were collected with all concentration units in μmol/L. (A hemoglobin concentration of 2.21 μmol/L is equal to 2.21×10^{-6} mol/L.)

$[Hb]_0$ (μmol/L)	$[CO]_0$ (μmol/L)	Initial Rate (μmol/L · s)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

a. Determine the orders of this reaction with respect to Hb and CO.
b. Determine the rate law.
c. Calculate the value of the rate constant.
d. What would be the initial rate for an experiment with $[Hb]_0 = 3.36$ μmol/L and $[CO]_0 = 2.40$ μmol/L?

36. The following data were obtained for the reaction

$2ClO_2(aq) + 2OH^-(aq) \longrightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$

where

$$\text{Rate} = -\frac{\Delta[ClO_2]}{\Delta t}$$

$[ClO_2]_0$ (mol/L)	$[OH^-]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

a. Determine the rate law and the value of the rate constant.
b. What would be the initial rate for an experiment with $[ClO_2]_0 = 0.175$ mol/L and $[OH^-]_0 = 0.0844$ mol/L?

Integrated Rate Laws

37. The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (s)	$[H_2O_2]$ (mol/L)
0	1.00
120 ± 1	0.91
300 ± 1	0.78
600 ± 1	0.59
1200 ± 1	0.37
1800 ± 1	0.22
2400 ± 1	0.13
3000 ± 1	0.082
3600 ± 1	0.050

Assuming that

$$\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

determine the rate law, the integrated rate law, and the value of the rate constant. Calculate $[H_2O_2]$ at 4000. s after the start of the reaction.

38. A certain reaction has the following general form:

$$aA \longrightarrow bB$$

At a particular temperature and $[A]_0 = 2.00 \times 10^{-2}$ *M*, concentration versus time data were collected for this reaction, and a plot of ln[A] versus time resulted in a straight line with a slope value of -2.97×10^{-2} min^{-1}.

a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
b. Calculate the half-life for this reaction.
c. How much time is required for the concentration of A to decrease to 2.50×10^{-3} *M*?

39. The rate of the reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C, the following data were collected:

Time (s)	$[NO_2]$ (mol/L)
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

Determine the rate law, the integrated rate law, and the value of the rate constant. Calculate $[NO_2]$ at 2.70×10^4 s after the start of the reaction.

40. A certain reaction has the following general form:

$$aA \longrightarrow bB$$

At a particular temperature and $[A]_0 = 2.80 \times 10^{-3}$ *M*, concentration versus time data were collected for this reaction, and a plot of 1/[A] versus time resulted in a straight line with a slope value of $+3.60 \times 10^{-2}$ L/mol · s.

a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
b. Calculate the half-life for this reaction.
c. How much time is required for the concentration of A to decrease to 7.00×10^{-4} *M*?

41. The decomposition of ethanol (C_2H_5OH) on an alumina (Al_2O_3) surface

$$C_2H_5OH(g) \longrightarrow C_2H_4(g) + H_2O(g)$$

was studied at 600 K. Concentration versus time data were collected for this reaction, and a plot of [A] versus time resulted in a straight line with a slope of -4.00×10^{-5} mol/L · s.

a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
b. If the initial concentration of C_2H_5OH was 1.25×10^{-2} *M*, calculate the half-life for this reaction.
c. How much time is required for all the 1.25×10^{-2} *M* C_2H_5OH to decompose?