(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.

14.22 The rate of disappearance of HCl was measured for the following reaction:

$$CH_3OH(aq) + HCl(aq) \longrightarrow CH_3Cl(aq) + H_2O(l)$$

The following data were collected:

Time (min)	[HCl] (M)
0.0	1.85
54.0	1.58
107.0	1.36
215.0	1.02
430.0	0.580

(a) Calculate the average rate of reaction, in M/s, for the time interval between each measurement. (b) Calculate the average rate of reaction for the entire time for the data from $t = 0.0$ min to $t = 430.0$ min.

(c) Graph [HCl] versus time and determine the instantaneous rates in M/min and M/s at $t = 75.0$ min and $t = 250$ min.

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?

14.26 (a) Consider the combustion of ethylene, $C_2H_4(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(g)$. If the concentration of C_2H_4 is decreasing at the rate of 0.036 M/s, what are the rates of change in the concentrations of CO_2 and H_2O? (b) The rate of decrease in N_2H_4 partial pressure in a closed reaction vessel from the reaction $N_2H_4(g) + H_2(g) \longrightarrow 2\,NH_3(g)$ is 74 torr per hour. What are the rates of change of NH_3 partial pressure and total pressure in the vessel?

RATE LAWS (section 14.3)

14.27 A reaction $A + B \longrightarrow C$ obeys the following rate law: Rate $= k[B]^2$. (a) If [A] is doubled, how will the rate change? Will the rate constant change? Explain. (b) What are the reaction orders for A and B? What is the overall reaction order? (c) What are the units of the rate constant?

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?

14.29 The decomposition reaction of N_2O_5 in carbon tetrachloride is $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$. The rate law is first order in N_2O_5. At 64 °C the rate constant is $4.82 \times 10^{-3}\,s^{-1}$. (a) Write the rate law for the reaction. (b) What is the rate of reaction when $[N_2O_5] = 0.0240\,M$? (c) What happens to the rate when the concentration of N_2O_5 is doubled to 0.0480 M? (d) What happens to the rate when the concentration of N_2O_5 is halved to 0.0120 M?

14.30 Consider the following reaction:

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

(a) The rate law for this reaction is first order in H_2 and second order in NO. Write the rate law. (b) If the rate constant for this reaction at 1000 K is $6.0 \times 10^4\,M^{-2}\,s^{-1}$, what is the reaction rate when $[NO] = 0.035\,M$ and $[H_2] = 0.015\,M$? (c) What is the reaction rate at 1000 K when the concentration of NO is increased to 0.10 M, while the concentration of H_2 is 0.010 M?

(d) What is the reaction rate at 1000 K if [NO] is decreased to 0.010 M and $[H_2]$ is increased to 0.030 M?

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?

14.33 The iodide ion reacts with hypochlorite ion (the active ingredient in chlorine bleaches) in the following way: $OCl^- + I^- \longrightarrow OI^- + Cl^-$. This rapid reaction gives the following rate data:

$[OCl^-]$ (M)	$[I^-]$ (M)	Initial Rate (M/s)
1.5×10^{-3}	1.5×10^{-3}	1.36×10^{-4}
3.0×10^{-3}	1.5×10^{-3}	2.72×10^{-4}
1.5×10^{-3}	3.0×10^{-3}	2.72×10^{-4}

(a) Write the rate law for this reaction. **(b)** Calculate the rate constant with proper units. **(c)** Calculate the rate when $[OCl^-] = 2.0 \times 10^{-3}$ M and $[I^-] = 5.0 \times 10^{-4}$ M.

14.34 The reaction $2\,ClO_2(aq) + 2\,OH^-(aq) \longrightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$ was studied with the following results:

Experiment	$[ClO_2]$ (M)	$[OH^-]$ (M)	Initial Rate (M/s)
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

(a) Determine the rate law for the reaction. **(b)** Calculate the rate constant with proper units. **(c)** Calculate the rate when $[ClO_2] = 0.100$ M and $[OH^-] = 0.050$ M.

14.35 The following data were measured for the reaction $BF_3(g) + NH_3(g) \longrightarrow F_3BNH_3(g)$:

Experiment	$[BF_3]$ (M)	$[NH_3]$ (M)	Initial Rate (M/s)
1	0.250	0.250	0.2130
2	0.250	0.125	0.1065
3	0.200	0.100	0.0682
4	0.350	0.100	0.1193
5	0.175	0.100	0.0596

(a) What is the rate law for the reaction? **(b)** What is the overall order of the reaction? **(c)** Calculate the rate constant with proper units? **(d)** What is the rate when $[BF_3] = 0.100$ M and $[NH_3] = 0.500$ M?

14.36 The following data were collected for the rate of disappearance of NO in the reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$:

Experiment	[NO] (M)	$[O_2]$ (M)	Initial Rate (M/s)
1	0.0126	0.0125	1.41×10^{-2}
2	0.0252	0.0125	5.64×10^{-2}
3	0.0252	0.0250	1.13×10^{-1}

(a) What is the rate law for the reaction? **(b)** What are the units of the rate constant? **(c)** What is the average value of the rate constant calculated from the three data sets? **(d)** What is the rate of disappearance of NO when [NO] = 0.0750 M and $[O_2] = 0.0100$ M? **(e)** What is the rate of disappearance of O_2 at the concentrations given in part (d)?

[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:

$$S_2O_8^{2-}(aq) + 3\,I^-(aq) \longrightarrow 2\,SO_4^{2-}(aq) + I_3^-(aq)$$

At a particular temperature the initial rate of disappearance of $S_2O_8^{2-}$ varies with reactant concentrations in the following manner:

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?