Solved Problems

INTRODUCTION

12.1. What is the difference between gas and gasoline?

Ans. Gas is a state of matter. Gasoline is a liquid, used mainly for fuel, with a nickname *gas*. Do not confuse the two. This chapter is about the gas phase, not about liquid gasoline.

12.2. What is a fluid?

Ans. A gas or a liquid.

PRESSURE OF GASES

12.3. Change 806 mmHg to (*a*) torr, (*b*) atmospheres, and (*c*) kilopascals.

Ans. (*a*) 806 torr (*b*) $806\text{ torr}\left(\frac{1\text{ atm}}{760\text{ torr}}\right) = 1.06\text{ atm}$ (*c*) $1.06\text{ atm}\left(\frac{101.3\text{ kPa}}{1\text{ atm}}\right) = 107\text{ kPa}$

12.4. Change (*a*) 703 torr to atmospheres, (*b*) 1.25 atm to torr, (*c*) 743 mmHg to torr, and (*d*) 1.01 atm to millimeters of mercury (mmHg).

Ans. (*a*) $703\text{ torr}\left(\frac{1\text{ atm}}{760\text{ torr}}\right) = 0.925\text{ atm}$ (*c*) $743\text{ mmHg}\left(\frac{1\text{ torr}}{1\text{ mmHg}}\right) = 743\text{ torr}$

(*b*) $1.25\text{ atm}\left(\frac{760\text{ torr}}{1\text{ atm}}\right) = 950\text{ torr}$ (*d*) $1.01\text{ atm}\left(\frac{760\text{ mmHg}}{1\text{ atm}}\right) = 768\text{ mmHg}$

12.5. How many pounds force does 1 atm pressure exert on the side of a metal can that measures 6.0 in. by 9.0 in.? (1 atm = 14.7 lb/in.^{2})

Ans.

$$\text{Area} = 6.0\text{ in.} \times 9.0\text{ in.} = 54\text{ in.}^2$$

$$54\text{ in.}^2\left(\frac{14.7\text{ lb}}{1\text{ in.}^2}\right) = 790\text{ lb} = 7.9 \times 10^2\text{ lb}$$

BOYLE'S LAW

12.6. What law may be stated qualitatively as "When you squeeze a gas, it gets smaller"?

Ans. Boyle's law

12.7. Calculate the product of the pressure and volume for each point in Table 12-1. What can you conclude?

Ans. $PV = 8.0$ L·atm in each case. You can conclude that PV is a constant for this sample of gas and that Boyle's law is obeyed.

12.8. If 4.00 L of gas at 1.22 atm is changed to 876 torr at constant temperature, what is its final volume?

Ans.

$$1.22\text{ atm}\left(\frac{760\text{ torr}}{1\text{ atm}}\right) = 927\text{ torr}$$

$$P_1V_1 = P_2V_2$$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{(927\text{ torr})(4.00\text{ L})}{876\text{ torr}} = 4.23\text{ L}$$

12.9. If 1.25 L of gas at 780 torr is changed to 965 mL at constant temperature, what is its final pressure?

Ans.

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(780\text{ torr})(1250\text{ mL})}{965\text{ mL}} = 1010\text{ torr}$$

12.10. A 1.00-L sample of gas at 25°C and 1.00-atm pressure is changed to 3.00-atm pressure at 25°C. What law may be used to determine its final volume?

Ans. Boyle's law may be used because the temperature is unchanged. Alternately, the combined gas law may be used, with 298 K, the Kelvin equivalent of 25°C, used for both T_1 and T_2.

12.11. A sample of gas occupies 2.48 L. What will be its new volume if its pressure is doubled at constant temperature?

Ans. According to Boyle's law, doubling the pressure will cut the volume in half; the new volume will be 1.24 L. A second method allows us to use unknown variables for the pressure:

	1	2
P	P_1	$P_2 = 2P_1$
V	2.48 L	V_2

$$V_2 = \frac{P_1V_1}{P_2} = \frac{P_1V_1}{2P_1} = \frac{V_1}{2} = \frac{2.48\ \text{L}}{2} = 1.24\ \text{L}$$

GRAPHICAL REPRESENTATION OF DATA

12.12. On a graph, what criteria represent direct proportionality?

Ans. The plot is a straight line and it passes through the origin.

12.13. What is the pressure of the gas described in Table 12-1 at 10.0 L? Answer first by calculating with Boyle's law, second by reading from Fig. 12-2, and third by reading from Fig. 12-3. Which determination is easiest (assuming that the graphs have already been drawn)?

Ans. The pressure of the gas is 0.80 atm. The second method involves merely reading a point from a graph. To use Fig. 12-3, you have to calculate the reciprocal of the pressure. None of the methods is difficult, however.

12.14. Plot the following data:

V (L)	*P* (atm)
1.50	4.00
3.00	2.00
6.00	1.00
12.00	0.500

Replot the data, using the volume and the reciprocal of the pressure. Do these values fall on a straight line? Are volume and the reciprocal of pressure directly proportional? Are volume and pressure directly proportional?

Ans. The points of the second plot fall on a straight line through the origin, and so the volume and reciprocal of pressure are directly proportional to each other, making the volume inversely proportional to the pressure.

CHARLES' LAW

12.15. Plot the following data:

V (L)	*t* (°C)
4.92	100
4.26	50
3.60	0
2.94	−50

Do the values fall on a straight line? Are volume and Celsius temperature directly proportional? Replot the volume versus the Kelvin temperature. Are volume and Kelvin temperature directly proportional?

Ans. The points of the first plot fall on a straight line, but that line does not go through the origin (the point at 0 L and 0°C), and so these quantities are *not* directly proportional. When volume is replotted versus Kelvin temperature, the resulting straight line goes through the origin, and thus volume and *absolute temperature* are directly proportional.

12.16. If 42.3 mL of gas at 22°C is changed to 44°C at constant pressure, what is its final volume?

Ans. Absolute temperatures must be used:

$$22°\text{C} + 273° = 295\text{ K}$$
$$44°\text{C} + 273° = 317\text{ K}$$

According to Charles' law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{(42.3\text{ mL})(317\text{ K})}{295\text{ K}} = 45.5\text{ mL}$$

Note that the volume is *not* doubled by doubling the Celsius temperature.

12.17. If 0.979 L of gas at 0°C is changed to 737 mL at constant pressure, what is its final temperature?

Ans. Using the reciprocal of the equation usually used for Charles' law:

$$\frac{T_2}{V_2} = \frac{T_1}{V_1}$$

and solving for T_2:

$$T_2 = \frac{T_1 V_2}{V_1} = \frac{(273\text{ K})(737\text{ mL})}{979\text{ mL}} = 206\text{ K}$$

The temperature was lowered to reduce the volume.

THE COMBINED GAS LAW

12.18. Calculate the missing value for each set of data in the following table:

	P_1	V_1	T_1	P_2	V_2	T_2
(*a*)	—	29.1 L	45°C	780 torr	2.22 L	77°C
(*b*)	12.0 atm	—	28°C	12.0 atm	750 mL	53°C
(*c*)	721 torr	200 mL	—	1.21 atm	0.850 L	100°C
(*d*)	1.00 atm	4.00 L	273 K	1.00 atm	2.00 L	—
(*e*)	7.00 atm	—	333 K	3.10 atm	6.00 L	444 K
(*f*)	1.00 atm	3.65 L	130°C	—	5.43 L	130°C

Ans. Each problem is solved by rearranging the equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

All temperatures must be in kelvins.

(*a*) $$P_1 = \frac{P_2 V_2 T_1}{T_2 V_1} = \frac{(780\text{ torr})(2.22\text{ L})(318\text{ K})}{(350\text{ K})(29.1\text{ L})} = 54.1\text{ torr}$$

(*b*) $$V_1 = \frac{P_2 V_2 T_1}{P_1 T_2} = \frac{(12.0\text{ atm})(750\text{ mL})(301\text{ K})}{(12.0\text{ atm})(326\text{ K})} = 692\text{ mL}$$

Since P did not change, Charles' law could have been used in the form

$$V_1 = \frac{V_2 T_1}{T_2}$$

(*c*) $$T_1 = \frac{P_1 V_1 T_2}{P_2 V_2} = \frac{(721\text{ torr})(0.200\text{ L})(373\text{ K})}{(1.21\text{ atm})(760\text{ torr/atm})(0.850\text{ L})} = 68.8\text{ K}$$

The units of P and V each must be the same in state 1 and state 2. Since each of them is given in diffferent units, one of each must be changed.

(*d*) $$T_2 = \frac{T_1 P_2 V_2}{P_1 V_1} = \frac{(273\text{ K})(1.00\text{ atm})(2.00\text{ L})}{(1.00\text{ atm})(4.00\text{ L})} = 137\text{ K}$$

(*e*) $$V_1 = \frac{P_2 V_2 T_1}{P_1 T_2} = \frac{(3.10\text{ atm})(6.00\text{ L})(333\text{ K})}{(7.00\text{ atm})(444\text{ K})} = 1.99\text{ L}$$

(*f*) $$P_2 = \frac{T_2 P_1 V_1}{T_1 V_2} = \frac{(403\text{ K})(1.00\text{ atm})(3.65\text{ L})}{(403\text{ K})(5.43\text{ L})} = 0.672\text{ atm}$$

Since $T_1 = T_2$, we could have used $P_2 = P_1 V_1 / V_2$ and arrived at the same answer.

12.19. A 9.00-L sample of gas has its pressure tripled while its absolute temperature is increased by 50%. What is its new volume?

Ans. Tripling P reduces the volume to 3.00 L. Then increasing T by 50% (multiplying it by 1.50) increases the volume by a factor of 1.50 to 4.50 L.

Alternatively:
$$V_2 = \left(\frac{P_1 V_1}{T_1}\right)\left(\frac{T_2}{P_2}\right) = \left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)(V_1)$$
$$= \left(\frac{1}{3}\right)\left(\frac{1.50}{1}\right)(9.00\text{ L}) = 4.50\text{ L}$$

THE IDEAL GAS LAW

12.20. Calculate R, the gas law constant, (*a*) in units of L·torr/(mol·K) and (b) in units of mL·atm/(mol·K).

Ans. (*a*) $$R = \frac{0.0821\text{ L·atm}}{\text{mol·K}}\left(\frac{760\text{ torr}}{1\text{ atm}}\right) = \frac{62.4\text{ L·torr}}{\text{mol·K}}$$

(*b*) $$R = \frac{0.0821\text{ L·atm}}{\text{mol·K}}\left(\frac{1000\text{ mL}}{1\text{ L}}\right) = \frac{82.1\text{ mL·atm}}{\text{mol·K}}$$

12.21. How can you recognize an ideal gas law problem?

Ans. Ideal gas law problems involve moles. If the number of moles of gas is given or asked for, or if a quantity that involves moles is given or asked for, the problem is most likely an ideal gas law problem. Thus, any problem involving masses of gas (which can be converted to moles of gas) or molar masses (grams per mole) or numbers of individual molecules (which can be converted to moles) and so forth is an ideal gas law problem. Problems that involve more than one temperature and/or one pressure of gas are most likely not ideal gas law problems.

12.22. Calculate the absolute temperature of 0.118 mol of a gas that occupies 10.0 L at 0.933 atm.

Ans. $$T = \frac{PV}{nR} = \frac{(0.933\text{ atm})(10.0\text{ L})}{(0.118\text{ mol})[0.0821\text{ L·atm/(mol·K)}]} = 963\text{ K}$$

12.23. Calculate the pressure of 0.0303 mol of a gas that occupies 1.24 L at 22°C.

Ans. $$P = \frac{nRT}{V} = \frac{(0.0303\text{ mol})[0.0821\text{ L·atm/(mol·K)}](295\text{ K})}{1.24\text{ L}} = 0.592\text{ atm}$$

12.24. Calculate the value of R if 1.00 mol of gas occupies 22.4 L at STP.

Ans. STP means 1.00 atm and 273 K (0°C). Thus,

$$R = \frac{PV}{nT} = \frac{(1.00\text{ atm})(22.4\text{ L})}{(1.00\text{ mol})(273\text{ K})} = 0.0821\text{ L·atm/(mol·K)}$$

12.25. Calculate the volume of 0.193 mol of a gas at 27°C and 825 torr.

Ans.
$$V = \frac{nRT}{P} = \frac{(0.193 \text{ mol})[0.0821 \text{ L·atm/(mol·K)}](300 \text{ K})}{(825 \text{ torr})(1 \text{ atm/760 torr})} = 4.38 \text{ L}$$

12.26. Calculate the volume of 1.00 mol of H_2O at 1.00-atm pressure and a temperature of 25°C.

Ans. Water (H_2O) is not a gas under these conditions, and so the equation $PV = nRT$ does not apply. (The ideal gas law can be used for water vapor, e.g., water over 100°C at 1 atm or water at lower temperatures mixed with air.) At 1-atm pressure and 25°C, water is a liquid with a density about 1.00 g/mL.

$$1.00 \text{ mol}\left(\frac{18.0 \text{ g}}{1 \text{ mol}}\right)\left(\frac{1 \text{ mL}}{1.00 \text{ g}}\right) = 18.0 \text{ mL}$$

12.27. Calculate the number of moles of a gas that occupies 4.00 L at 303 K and 1.12 atm.

Ans.
$$n = \frac{PV}{RT} = \frac{(1.12 \text{ atm})(4.00 \text{ L})}{[0.0821 \text{ L·atm/(mol·K)}](303 \text{ K})} = 0.180 \text{ mol}$$

12.28. Calculate the number of moles of gas present in Problem 12.18*d*.

Ans. Since the number of moles of gas does not change during the process of changing from state 1 to state 2, either set of data can be used to calculate the number of moles of gas. Since all three values are given for state 1, it is easier to use that state:

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(4.00 \text{ L})}{[0.0821 \text{ L·atm/(mol·K)}](273 \text{ K})} = 0.178 \text{ mol}$$

12.29. (*a*) Compare qualitatively the volumes at STP of 6.8 mol N_2 and 6.8 mol H_2. (*b*) Compare the volumes at STP of 6.8 g N_2 and 6.8 g H_2.

Ans. (*a*) Since the pressures, temperature, and numbers of moles are the same, the volumes also must be the same. (*b*) The number of moles of nitrogen is less than the number of moles of hydrogen because its molar mass is greater. Since the number of moles of nitrogen is less, so is its volume.

12.30. Calculate the volume of 7.07 g of helium at 27°C and 1.00 atm.

Ans.
$$7.07 \text{ g He}\left(\frac{1 \text{ mol He}}{4.00 \text{ g He}}\right) = 1.77 \text{ mol He}$$

$$V = \frac{nRT}{P} = \frac{(1.77 \text{ mol})[0.0821 \text{ L·atm/(mol·K)}](300 \text{ K})}{1.00 \text{ atm}} = 43.6 \text{ L}$$

12.31. Repeat the prior problem, using hydrogen gas instead of helium. Explain why the occurrence of hydrogen gas in diatomic molecules is so important.

Ans.
$$n = 3.51 \text{ mol} \qquad V = 86.5 \text{ L}$$

The gas laws work with moles of *molecules*, not atoms. It is necessary to know that hydrogen gas occurs in diatomic molecules so that the proper number of moles of gas may be calculated from the mass of the gas.

DALTON'S LAW OF PARTIAL PRESSURES

12.32. What is the total pressure of a gas mixture containing He at 0.173 atm, Ne at 0.201 atm, and Ar at 0.550 atm?

Ans.
$$P_{total} = P_{He} + P_{Ne} + P_{Ar} = 0.173 \text{ atm} + 0.201 \text{ atm} + 0.550 \text{ atm} = 0.924 \text{ atm}$$

12.33. What is the pressure of H_2 if 0.250 mol of H_2 and 0.120 mol of He are placed in a 10.0-L vessel at 27°C?

Ans. The presence of He makes no difference. The pressure of H_2 is calculated with the ideal gas law, using the number of moles of H_2.

$$P = \frac{nRT}{V} = \frac{(0.250 \text{ mol})[0.0821 \text{ L·atm/(mol·K)}](300 \text{ K})}{10.0 \text{ L}} = 0.616 \text{ atm}$$

12.34. What is the total pressure of a gas mixture containing H_2 at 0.173 atm, N_2 at 0.201 atm, and NO at 0.550 atm?

Ans.
$$P_{total} = P_{H_2} + P_{N_2} + P_{NO} = 0.924 \text{ atm}$$

12.35. What is the difference between Problems 12.32 and 12.34?

Ans. In Problem 12.34, molecules are involved. In Problem 12.32, uncombined atoms are involved. In both cases, the same laws apply, and it is best to regard an uncombined atom of He, for example, as a monatomic molecule.

12.36. The total pressure of a 125-mL sample of oxygen collected over water at 25°C is 1.030 atm. (*a*) How many moles of gas are present? (*b*) How many moles of water vapor are present? (*c*) How many moles of oxygen are present?

Ans. (*a*) $n = \frac{PV}{RT} = \frac{(1.030 \text{ atm})(0.125 \text{ L})}{[0.0821 \text{ L·atm/(mol·K)}](298 \text{ K})} = 5.26 \times 10^{-3} \text{ mol total}$

(*b*) The gas is composed of O_2 and water vapor. The pressure of the water vapor at 25°C, given in the last part of Sec. 12.8 or in tables in your text, is 24 torr. In atmospheres:

$$24 \text{ torr}\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.032 \text{ atm}$$

$$n_{H_2O} = \frac{PV}{RT} = \frac{(0.032 \text{ atm})(0.125 \text{ L})}{[0.0821 \text{ L·atm/(mol·K)}](298 \text{ K})} = 1.6 \times 10^{-4} \text{ mol } H_2O$$

(*c*) The pressure of the O_2 is therefore

$$1.030 \text{ atm} - 0.032 \text{ atm} = 0.998 \text{ atm}$$

$$n_{O_2} = \frac{PV}{RT} = \frac{(0.998 \text{ atm})(0.125 \text{ L})}{[0.0821 \text{ L·atm/(mol·K)}](298 \text{ K})} = 5.10 \times 10^{-3} \text{ mol } O_2$$

Check : $5.10 \times 10^{-3} \text{ mol} + 0.16 \times 10^{-3} \text{ mol} = 5.26 \times 10^{-3} \text{ mol}$

12.37. In Dalton's law problems, what is the difference in behavior of water vapor mixed with air compared to helium mixed with air?

Ans. The pressure of water vapor, if it is in contact with liquid water, is governed by the temperature only. More water can evaporate or some water vapor can condense if the pressure is not equal to the tabulated vapor pressure at the given temperature. Helium is a gas under most conditions and is not capable of adjusting its pressure in the same way.

Supplementary Problems

12.38. Explain why gas law problems are not given with data to four or five significant figures.

Ans. The laws are only approximate, and having better data would not necessarily yield more accurate answers.

12.39. A mixture of gases contains He, Ne, and Ar. The pressure of He is 0.300 atm. The volume of Ne is 4.00 L. The temperature of Ar is 27°C. What value can be calculated from these data? Explain.

Ans. The temperature of Ar is the temperature of all the gases, since they are all mixed together. The volume of Ne is the volume of each of the gases and the total volume, too. Therefore, the number of moles of He can be calculated because its pressure is also known:

$$n = \frac{PV}{RT} = \frac{(0.300 \text{ atm})(4.00 \text{ L})}{[0.0821 \text{ L·atm/(mol·K)}](300 \text{ K})} = 0.0487 \text{ mol He}$$

12.40. Under what conditions of temperature and pressure do the gas laws work best?

Ans. Under low-pressure and high-temperature conditions (far from the possibility of change to the liquid state).

12.41. If 0.223 g of a gas occupies 2.87 L at 17°C and 700 torr, what is the identity of the gas?

Ans. If you do not see at first how to solve this problem to completion, at least you can recognize that P, V, and T data are given. First calculate the number of moles of gas present:

$$700\ \text{torr}\left(\frac{1\ \text{atm}}{760\ \text{torr}}\right) = 0.921\ \text{atm} \qquad 17°\text{C} = (17 + 273)\ \text{K} = 290\ \text{K}$$

$$n = \frac{PV}{RT} = \frac{(0.921\ \text{atm})(2.87\ \text{L})}{[0.0821\ \text{L·atm/(mol·K)}](290\ \text{K})} = 0.111\ \text{mol}$$

We now know the mass of the gas and the number of moles. That is enough to calculate the molar mass:

$$\frac{0.223\ \text{g}}{0.111\ \text{mol}} = 2.01\ \text{g/mol}$$

The gas has a molar mass of 2.01 g/mol. It could only be hydrogen, H_2, because no other gas has a molar mass that low.

12.42. Which temperature scale must be used in (*a*) Boyle's law problems, (*b*) ideal gas law problems, (*c*) combined gas law problems, and (*d*) Charles' law problems?

Ans. (*a*) No temperature is used in the calculations for Boyle's law problems since the temperature must be constant. (*b*) through (*d*) Kelvin.

12.43. The total pressure of a mixture of gases is 1.50 atm. The mixture contains 0.10 mol of N_2 and 0.20 mol of O_2. What is the partial pressure of O_2?

Ans. The oxygen in the mixture is two-thirds of the number of moles, so it exerts two-thirds of the total pressure—1.00 atm. Or

$$\frac{n_{N_2}}{n_{O_2}} = \frac{0.10\ \text{mol N}_2}{0.20\ \text{mol O}_2} = \frac{P_{N_2}V/(RT)}{P_{O_2}V/(RT)} = \frac{P_{N_2}}{P_{O_2}} = 0.50$$

$$P_{N_2} = 0.50P_{O_2}$$

$$P_{N_2} + P_{O_2} = 1.50\ \text{atm}$$

$$0.50P_{O_2} + P_{O_2} = 1.50P_{O_2} = 1.50\ \text{atm}$$

$$P_{O_2} = \frac{1.50\ \text{atm}}{1.50} = 1.00\ \text{atm}$$

12.44. Calculate the mass of $KClO_3$ required to decompose to provide 0.728 L of O_2 at 20°C and 1.02 atm.

Ans. The volume, temperature, and pressure given allow us to calculate the number of moles of *oxygen*:

$$n_{O_2} = \frac{PV}{RT} = \frac{(1.02\ \text{atm})(0.728\ \text{L})}{[0.0821\ \text{L·atm/(mol·K)}](293\ \text{K})} = 0.0309\ \text{mol}$$

The number of moles of $KClO_3$ may be calculated from the number of moles of O_2 by means of the balanced chemical equation, and that value is then converted to mass.

$$2\ \text{KClO}_3 \longrightarrow 2\ \text{KCl} + 3\ \text{O}_2$$

$$0.0309\ \text{mol O}_2\left(\frac{2\ \text{mol KClO}_3}{3\ \text{mol O}_2}\right)\left(\frac{122\ \text{g KClO}_3}{1\ \text{mol KClO}_3}\right) = 2.51\ \text{g KClO}_3$$

12.45. Two samples of gas at equal pressures and temperatures are held in containers of equal volume. What can be stated about the comparative number of molecules in each gas sample?

Ans. Since the volumes, temperatures, and pressures are the same, the numbers of moles of the two gases are the same. Therefore, there are equal numbers of molecules of the two gases.

12.46. P is inversely proportional to V. Write three mathematical expressions that relate this fact.

Ans.
$$P \propto \frac{1}{V} \qquad P = \frac{k}{V} \qquad PV = k$$

12.47. Write an equation for the combined gas law, using temperature in degrees Celsius. Explain why the Kelvin scale is more convenient.

Ans.
$$\frac{P_1V_1}{t_1 + 273} = \frac{P_2V_2}{t_2 + 273}$$

The law is simpler with the Kelvin temperatures.

12.48. Calculate the molar mass of a gas if 12.6 g occupies 5.11 L at 1.12 atm and 22°C.

Ans. From the pressure, volume, and temperature data, we can calculate the number of moles of gas present. From the number of moles and the mass, we can calculate the molar mass.

$$n = \frac{PV}{RT} = \frac{(1.12\text{ atm})(5.11\text{ L})}{[0.0821\text{ L·atm/(mol·K)}](295\text{ K})} = 0.236\text{ mol}$$

$$\text{Molar mass} = 12.6\text{ g}/0.236\text{ mol} = 53.4\text{ g/mol}$$

12.49. What volume of a CO_2 and H_2O mixture at 1.00 atm and 450 K can be prepared by the thermal decomposition of 0.950 g $NaHCO_3$?

$$2\,NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + CO_2 + H_2O(g)$$

Ans.
$$0.950\text{ g NaHCO}_3\left(\frac{1\text{ mol NaHCO}_3}{84.0\text{ g NaHCO}_3}\right)\left(\frac{1\text{ mol CO}_2}{2\text{ mol NaHCO}_3}\right) = 5.65 \times 10^{-3}\text{ mol CO}_2$$

The same number of moles of gaseous water (at 450 K) is obtained. The total number of moles of gas is 0.0113 mol. The volume is given by

$$V = \frac{nRT}{P} = \frac{(0.0113\text{ mol})[0.0821\text{ L·atm/(mol·K)}](450\text{ K})}{1.00\text{ atm}} = 0.417\text{ L}$$

Note: At 450 K and 1.00 atm, water is completely in the gas phase. (The vapor pressure of water at 450 K is greater than 1.00 atm.)

12.50. What volume of O_2 at STP can be prepared by the thermal decomposition of 0.500 g of Hg_2O?

Ans.
$$2\,Hg_2O \xrightarrow{\text{heat}} 4\,Hg + O_2$$

$$0.500\text{ g Hg}_2\text{O}\left(\frac{1\text{ mol Hg}_2\text{O}}{416\text{ g Hg}_2\text{O}}\right)\left(\frac{1\text{ mol O}_2}{2\text{ mol Hg}_2\text{O}}\right) = 6.01 \times 10^{-4}\text{ mol O}_2$$

$$V = \frac{nRT}{P} = \frac{(6.01 \times 10^{-4}\text{ mol})[0.0821\text{ L·atm/(mol·K)}](273\text{ K})}{1.00\text{ atm}} = 0.0135\text{ L}$$

12.51. What volume will 14.3 g of CH_4 occupy at 38°C and 0.888 atm?

Ans.
$$14.3\text{ g CH}_4\left(\frac{1\text{ mol CH}_4}{16.0\text{ g CH}_4}\right) = 0.894\text{ mol CH}_4$$

$$V = \frac{nRT}{P} = \frac{(0.894\text{ mol})[0.0821\text{ L·atm/(mol·K)}](311\text{ K})}{0.950\text{ atm}} = 24.0\text{ L}$$

12.52. Show that the volumes of individual gases involved in a chemical reaction (before they are mixed or after they are separated), all measured at the same temperature and pressure, are in proportion to their numbers of moles. Use the following reaction as an example:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

Ans.
$$\frac{n_{O_2}}{n_{CO}} = \frac{PV_{O_2}/(RT)}{PV_{CO}/(RT)} = \frac{V_{O_2}}{V_{CO}}$$

If gas *mixtures* were involved, their volumes would necessarily be the same and their *pressures* would be in the ratios of their numbers of moles.

12.53. What is the ratio of volume of CO_2 produced to O_2 used up, both at the same temperature and pressure, for the reaction in the prior problem?

Ans. The ratio is 2 : 1, as in the balanced equation.

12.54. (*a*) Calculate the initial volume of 3.00 L of gas whose pressure has been increased from 1.00 atm to 2.00 atm.
(*b*) Calculate the final volume of 3.00 L of gas whose pressure has been increased from 1.00 atm to 2.00 atm.

Ans. Read the problem carefully. What must be assumed in part (*a*)? in part (*b*)? Since no mention was made of temperature, we must assume that the temperature is constant in both parts, or we cannot do the problem.

(*a*) The initial volume was asked for, so we must assume that 3.00 L is the final volume.

$$V_1 = \frac{V_2 P_2}{P_1} = \frac{(3.00\ \text{L})(2.00\ \text{atm})}{1.00\ \text{atm}} = 6.00\ \text{L}$$

(*b*) The final volume was asked for, so 3.00 L must be the initial volume.

$$V_2 = \frac{V_1 P_1}{P_2} = \frac{(3.00\ \text{L})(1.00\ \text{atm})}{2.00\ \text{atm}} = 1.50\ \text{L}$$

(In each case, doubling the pressure reduced the volume to one-half its initial volume.)

12.55. Calculate the final volume of 1.20 L of gas whose pressure is halved at constant temperature.

Ans. The final volume is 2.40 L. According to Boyle's law, halving the pressure causes V to be doubled.

12.56. In a certain experiment, when 2.500 g of $KClO_3$ was heated, some O_2 was driven off. After the experiment, 2.402 g of solid was left. (Not all the $KClO_3$ decomposed.) (*a*) Write a balanced chemical equation for the reaction. (*b*) What compounds make up the solid? (*c*) What causes the loss of mass of the sample? (*d*) Calculate the volume of oxygen produced at STP.

Ans. (*a*) $2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$

(*b*) The solid is KCl and unreacted $KClO_3$.

(*c*) The loss of mass is caused solely by the escape of O_2.

(*d*) $0.098\ \text{g}\ O_2\left(\frac{1\ \text{mol}\ O_2}{32.0\ \text{g}\ O_2}\right) = 0.0031\ \text{mol}\ O_2$

$$V = \frac{nRT}{P} = \frac{(0.0031\ \text{mol})[0.0821\ \text{L·atm/(mol·K)}](273\ \text{K})}{1.00\ \text{atm}} = 0.069\ \text{L} = 69\ \text{mL}$$

12.57. Calculate the ratios of volume to Celsius temperature for the data in Table 12-3. Are the ratios the same for all the temperatures?

Ans. No

12.58. Replot the data of Table 12-1, using P and $1/V$. Is the result a straight line? Explain.

Ans. The result is still a straight line. $PV = k$ so $P = k(1/V)$ and also $V = k(1/P)$.

12.59. What is the final temperature or pressure in each of the following parts: (*a*) The pressure of a sample of gas at STP is raised 2 atm. (*b*) The pressure of a sample of gas at STP is raised to 2 atm. (*c*) The temperature of a sample of gas at STP is raised 20°C. (*d*) The temperature of a sample of gas at STP is raised to 20°C?

Ans. (*a*) 3 atm (*b*) 2 atm (*c*) 20°C (*d*) 20°C

12.60. For a mixture of two gases, gas 1 and gas 2, put in equals signs or plus signs in the appropriate places in the equations below:

$$P_{\text{total}} = P_1 \quad P_2 \qquad T_{\text{total}} = T_1 \quad T_2$$
$$V_{\text{total}} = V_1 \quad V_2 \qquad n_{\text{total}} = n_1 \quad n_2$$

Ans.

$$P_{\text{total}} = P_1 + P_2 \qquad T_{\text{total}} = T_1 = T_2$$
$$V_{\text{total}} = V_1 = V_2 \qquad n_{\text{total}} = n_1 + n_2$$

12.61. Draw a figure to represent all the conversions learned so far, including volumes of gases. Start with the figure you did for Problem 11.31.

Ans. The figure is presented on p. 348.

CHAPTER 13

Kinetic Molecular Theory

13.1 INTRODUCTION

In Chap. 12 laws governing the behavior of gases were presented. The fact that gases exert pressure was stated, but no reasons why gases should exhibit such behavior were given. The *kinetic molecular theory* (KMT) explains the gas laws that we have studied and some additional ones. It describes gases in terms of the behavior of the molecules that make them up. (The noble gases exist as individual atoms, but for purposes of explaining the KMT they will be included and treated as molecules. They may be thought of as monatomic molecules.)

13.2 POSTULATES OF THE KINETIC MOLECULAR THEORY

All gases, under ordinary conditions of temperature and pressure, are made of molecules (including one-atom molecules such as are present in samples of the noble gases). That is, ionic substances do not form gases under conditions prevalent on earth. The molecules of a gas act according to the following postulates:

1. Molecules are in constant random motion.
2. The molecules exhibit negligible intermolecular attractions or repulsions except when they collide.
3. Their collisions are elastic, which means that although the molecules transfer energy from one to another, they do not lose kinetic energy when they collide with one another or with the walls of their container.
4. The gas molecules occupy a negligible fraction of the volume occupied by the gas as a whole.
5. The average *kinetic energy* of the gas molecules is directly proportional to the *absolute* temperature of the gas:

$$\overline{KE} = \frac{3}{2}kT = \frac{1}{2}m\overline{v^2}$$

The bars mean "average." The k in the proportionality constant is called the *Boltzmann constant*. It is the ideal gas law constant (with unfamiliar units), divided by Avogadro's number. Note that this is the same for all gases.

Postulate 1 means that molecules move in any direction whatsoever until they collide with another molecule or a wall, whereupon they bounce off and move in another direction until their next collision. Postulate 2 means that the molecules move in a straight line at constant speed between collisions. Postulate 3 means that there is no friction in molecular collisions. The molecules have the same total kinetic energy after each collision as before. Postulate 4 concerns the volume of the molecule themselves versus the volume of the container they occupy. The individual particles do not occupy the entire container. If the molecules of gas had zero volumes and zero intermolecular attractions and repulsions, the gas would obey the ideal gas law exactly. Postulate 5 means that if two gases are at the same temperature, their molecules will have the same average kinetic energies.

EXAMPLE 13.1. Calculate the value for k, the Boltzmann constant, using the following value for R:

$$R = 8.31\ \text{J/(mol·K)}$$

Ans.

$$k = \frac{R}{N} = \frac{8.31\ \text{J/(mol·K)}}{6.02 \times 10^{23}\ \text{molecules/mol}} = \frac{1.38 \times 10^{-23}\ \text{J}}{\text{molecule·K}}$$

EXAMPLE 13.2. Calculate the average kinetic energy of H_2 molecules at 1.00 atm and 300 K.

Ans.

$$\overline{\text{KE}} = \tfrac{3}{2}kT = 1.5[1.38 \times 10^{-23}\ \text{J/(molecule·K)}](300\ \text{K}) = 6.21 \times 10^{-21}\ \text{J}$$

13.3. EXPLANATION OF GAS PRESSURE, BOYLE'S LAW, AND CHARLES' LAW

Kinetic molecular theory explains why gases exert pressure. The constant bombardment of the walls of the vessel by the gas molecules, like the hitting of a target by machine gun bullets, causes a constant force to be applied to the wall. The force applied, divided by the area of the wall, is the pressure of the gas.

Boyle's law may be explained using the kinetic molecular theory by considering the box illustrated in Fig. 13-1. If a sample of gas is placed in the left half of the box shown in the figure, it will exert a certain pressure. If the volume is doubled by extending the right wall to include the entire box shown in the figure, the pressure should fall to one-half its original value. Why should that happen? In an oversimplified picture, the molecules bouncing back and forth between the right and left walls now have twice as far to travel, and thus they hit each wall only one-half as often in a given time. Therefore, the pressure is only one-half what it was. How about the molecules that are traveling up and down or in and out? There are as many such molecules as there were before, and they hit the walls as often; but they are now striking an area twice as large, and so the pressure is one-half what it was originally. Thus, doubling the volume halves the pressure. This can be shown to be true no matter what the shape of the container.

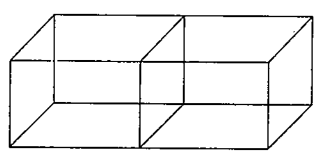


Fig. 13-1. Explanation of Boyle's law

Charles' law governs the volume of a gas at constant pressure when its temperature is changed. When the absolute temperature of a gas is multiplied by 4, for example, the average kinetic energy of its molecules is also multiplied by 4 (postulate 5). The kinetic energy of any particle is given by $\text{KE} = \frac{1}{2}mv^2$, where m is the mass of the particle and v is its velocity. When the kinetic energy is multiplied by 4, what happens to the velocity? It is doubled. (Since the v term is being squared, to effect a fourfold increase, you need only to double the velocity: $2^2 = 4$.)

$$\text{KE}_1 = \tfrac{1}{2}m{v_1}^2$$

$$\text{KE}_2 = \tfrac{1}{2}m{v_2}^2 = 4\text{KE}_1 = \tfrac{1}{2}m(2v_1)^2$$

The velocity v_2 is equal to $2v_1$. On average, in a sample of gas the molecules are going twice as fast at the higher temperature. They therefore hit the walls (1) twice as often per unit time and (2) twice as hard each time they hit, for a combined effect of 4 times the pressure (in a given volume). If we want a constant pressure, we have to expand the volume to 4 times what it was before, and we see that multiplying the absolute temperature by 4 must be accompanied by a fourfold increase in volume if the pressure is to be kept constant.

13.4. GRAHAM'S LAW

An experimental law not yet discussed is *Graham's law*, which states that the rate of effusion or diffusion of a gas is inversely proportional to the square root of its molar mass. *Effusion* is the passage of a gas through small holes in its container, such as the pores in a porous cup. The deflation of a helium-filled party balloon over several days results from the helium atoms effusing through the tiny pores of the balloon wall. *Diffusion* is the passage of a gas through another gas. For example, if a bottle of ammonia water is spilled in one corner of a room, the odor of ammonia is soon apparent throughout the room. The ammonia molecules have diffused through the air molecules. Consider two gases with molar masses MM_1 and MM_2. The ratio of their rates of effusion or diffusion is given by

$$\frac{r_1}{r_2} = \sqrt{\frac{MM_2}{MM_1}}$$

That is, the heavier a molecule of the gas, the more slowly it effuses or diffuses.

The rate of effusion or diffusion of a gas is directly proportional to the "average" velocity of its molecules.

EXAMPLE 13.3. A sample of nitrogen and a sample of neon are both at the same temperature. What is the ratio of the "average" velocities of their molecules?

Ans. Since the temperatures are the same, so are the average kinetic energies of their molecules. From Graham's law,

$$\frac{v_{Ne}}{v_{nitrogen}} = \sqrt{\frac{MM_{nitrogen}}{MM_{Ne}}} = \sqrt{\frac{28.0}{20.2}} = 1.18$$

The neon atoms are moving 1.18 times as fast as the (heavier) nitrogen molecules.

Graham's law may be explained in terms of the kinetic molecular theory as follows: Since two gases are at the same temperature, their average kinetic energies are the same:

$$\overline{KE_1} = \overline{KE_2} = \tfrac{1}{2}m_1\overline{v_1^2} = \tfrac{1}{2}m_2\overline{v_2^2}$$

Multiplying the last of these equations by 2 yields

$$m_1\overline{v_1^2} = m_2\overline{v_2^2} \qquad \text{or} \qquad \frac{m_1}{m_2} = \frac{\overline{v_2^2}}{\overline{v_1^2}}$$

Since the masses of the molecules are proportional to their molar masses, and the average velocity of the molecules is a measure of the rate of effusion or diffusion, all we have to do to this equation to get Graham's law is to take its square root. (The square root of $\overline{v^2}$ is not quite equal to the average velocity, but is a quantity called the *root mean square velocity*. See Problem 13.17.)

Solved Problems

POSTULATES OF THE KINETIC MOLECULAR THEORY

13.1. (*a*) Calculate the volume at 100°C of 18.0 g of liquid water, assuming the density to be 1.00 g/mL. (*b*) Calculate the volume of 18.0 g of water vapor at 100°C and 1.00-atm pressure, using the ideal gas law. (*c*) Assuming that the volume of the liquid is the total volume of the molecules themselves, calculate the percentage of the gas volume occupied by molecules.

Ans. (*a*) $18.0\text{ g}\left(\frac{1.00\text{ mL}}{1.00\text{ g}}\right) = 18.0\text{ mL} = 0.0180\text{ L}$

(*b*) $V = \frac{nRT}{P} = \frac{(1.00\text{ mol})[0.0821\text{ L·atm/(mol·K)}](373\text{ K})}{1.00\text{ atm}} = 30.6\text{ L}$

(*c*) The percentage occupied by the molecules is

$$\frac{0.0180\text{ L}}{30.6\text{ L}} \times 100\% = 0.0588\%$$

13.2. If two different gases are at the same temperature, which of the following must also be equal, (*a*) their pressures, (*b*) their average molecular velocities, or (*c*) the average kinetic energies of their molecules?

Ans. (*c*) Their average kinetic energies must be equal since the temperatures are equal.

13.3. Does the kinetic molecular theory state that all the molecules of a given sample of gas have the same velocity since they are all at one temperature?

Ans. No. The kinetic molecular theory states that the *average* kinetic energy is related to the temperature, not the velocity or kinetic energy of any one molecule. The velocity of each individual molecule changes as it strikes other molecules or the walls.

13.4. Calculate the temperature at which CO_2 molecules have the same "average" velocity as nitrogen molecules have at 273 K.

Ans. Let

$$\overline{v^2} = \overline{v_{N_2}^2} = \overline{v_{CO_2}^2}$$

$$\frac{T_{CO_2}}{T_{N_2}} = \frac{\overline{KE_{CO_2}}}{\overline{KE_{N_2}}} = \frac{m_{CO_2}\overline{v^2}}{m_{N_2}\overline{v^2}} = \frac{m_{CO_2}}{m_{N_2}} = \frac{44.0}{28.0} = 1.57$$

$$T_{CO_2} = 1.57T_{N_2} = 1.57(273\ \text{K}) = 429\ \text{K}$$

13.5. If the molecules of a gas are compressed so that their average distance of separation gets smaller, what should happen to the forces between them? To their ideal behavior?

Ans. As the average distance gets smaller, the intermolecular forces increase. As the intermolecular forces increase and the volume of the molecules themselves becomes a more significant fraction of the total gas volume, their behavior becomes further from ideal.

EXPLANATION OF GAS PRESSURE, BOYLE'S LAW, AND CHARLES' LAW

13.6. Suppose that we double the length of each side of a rectangular box containing a gas. (*a*) What will happen to the volume? (*b*) What will happen to the pressure? (*c*) Explain the effect on the pressure on the basis of the kinetic molecular theory.

Ans. (*a*) The volume will increase by a factor of $(2)^3 = 8$. (*b*) The pressure will fall to one-eighth its original value. (*c*) In each direction, the molecules will hit the wall only one-half as often, and the force on each wall will drop to one-half of what it was originally because of this effect. Each wall has 4 times the area, and so the pressure will be reduced to one-fourth its original value because of this effect. The total reduction in pressure is $\frac{1}{2} \times \frac{1}{4} = \frac{1}{8}$, in agreement with Boyle's law.

GRAHAM'S LAW

13.7. (*a*) If the velocity of a single gas molecule doubles, what happens to its kinetic energy? (*b*) If the average velocity of the molecules of a gas doubles, what happens to the temperature of the gas?

Ans. (*a*)

$$v_2 = 2v_1$$

$$KE_2 = \tfrac{1}{2}mv_2^2 = \tfrac{1}{2}m(2v_1)^2 = 4\left(\tfrac{1}{2}mv_1^2\right) = 4\ KE_1$$

The kinetic energy is increased by a factor of 4.

(*b*) The absolute temperature is increased by a factor of 4.

13.8. Would it be possible to separate isotopes by using the principle of Graham's law? Explain what factors would be important.

Ans. Since the molecules containing different isotopes have different masses, it is possible to separate them on the basis of their different "average" molecular velocities. One would have to have gaseous molecules in which the element being separated into its isotopes was the only element present in more than one isotope. For example, if uranium is being separated, a gaseous compound of uranium is needed. The compound could be made with chlorine perhaps, but chlorine exists naturally in two isotopes of its own, and many different masses of molecules could be prepared with the naturally occurring mixture. Naturally occurring fluorine exists 100% as ^{19}F, and molecules of its gaseous compound with uranium, UF_6, will have two different masses, corresponding to $^{235}UF_6$ and $^{238}UF_6$. Uranium has been separated into its isotopes by repeated effusion of UF_6 through towers of porous dividers. Each process enriches the individual isotopes a little, and very many repetitions are required to get relatively pure isotopes.

13.9. Calculate the ratio of rates of effusion of $^{238}UF_6$ and $^{235}UF_6$. Fluorine is 100% ^{19}F.

Ans. The masses of the molecules are 352 and 349 amu. The relative rates of effusion are

$$\sqrt{\frac{352}{349}} = 1.004$$

The molecules of $^{235}UF_6$ will travel on average 1.004 times as fast as those of $^{238}UF_6$.

13.10. List the different molecular masses possible in UCl_3 with ^{238}U and ^{235}U as well as ^{35}Cl and ^{37}Cl.

Ans.

$^{238}U(^{35}Cl)_3$	343 amu	$^{235}U(^{35}Cl)_3$	340 amu
$^{238}U(^{35}Cl)_2(^{37}Cl)$	345 amu	$^{235}U(^{35}Cl)_2(^{37}Cl)$	342 amu
$^{238}U(^{35}Cl)(^{37}Cl)_2$	347 amu	$^{235}U(^{35}Cl)(^{37}Cl)_2$	344 amu
$^{238}U(^{37}Cl)_3$	349 amu	$^{235}U(^{37}Cl)_3$	346 amu

13.11. What possible complications would there be in trying to separate hydrogen into ^1H and ^2H by gaseous diffusion?

Ans. Hydrogen occurs as diatomic molecules, and it would be easy to separate $^1H_2$, $^1H^2H$, and $^2H_2$, but not the individual atoms. There would be very little $^2H_2$ since the heavy isotope accounts for only 0.015% of naturally occurring hydrogen atoms.

Supplementary Problems

13.12. (*a*) Is the ratio

$$\frac{\text{Total volume of gas molecules}}{\text{Volume of gas sample}}$$

smaller for a given sample of gas at constant pressure at 300 K or at 400 K? (*b*) Will the gas exhibit more ideal behavior at 300 K or at 400 K?

Ans. (*a*) The ratio is smaller at 400 K. The volume of the molecules themselves does not change appreciably between the two temperatures, but the gas volume changes according to Charles' law.

(*b*) Since the gas volume is larger at 400 K, the gas molecules are farther apart at that temperature and exhibit lower intermolecular forces. The gas is therefore more ideal at the higher temperature.

13.13. (*a*) Is the ratio

$$\frac{\text{Total volume of gas molecules}}{\text{Volume of gas sample}}$$

smaller for a given sample of gas at constant temperature at 1.00 atm or at 2.00 atm? (*b*) Will the gas exhibit more ideal behavior at 1.00 atm or at 2.00 atm?

Ans. (*a*) The ratio is smaller at 1.00 atm. The volume of the molecules themselves does not change appreciably between the two pressures, but the gas volume changes according to Boyle's law.

(*b*) Since the gas volume is larger at 1.00 atm, the gas molecules are farther apart at that temperature, and exhibit lower intermolecular forces. The gas is therefore more ideal at the lower pressure.

13.14. (*a*) Calculate the average kinetic energy of O_2 molecules at 1.00 atm and 300 K. (*b*) Does the pressure matter? (*c*) Does the identity of the gas matter?

Ans. (*a*)

$$\overline{KE} = \tfrac{3}{2}kT = 1.5[1.38 \times 10^{-23}\ \text{J/(molecule·K)}](300\ \text{K}) = 6.21 \times 10^{-21}\ \text{J}$$

(*b*) and (*c*) The pressure and the identity of the gas do not matter.

13.15. (*a*) Calculate the "average" velocity of O_2 molecules at 1.00 atm and 300 K. (*b*) Does the pressure matter? (*c*) Does the identity of the gas matter?

Ans. (*a*)

$$\tfrac{1}{2}m\overline{v^2} = 6.21 \times 10^{-21}\text{ J} \quad \text{(from the prior problem)}$$

$$m_{O_2} = 32.0\text{ amu}\left(\frac{1\text{ g}}{6.02 \times 10^{23}\text{ amu}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right) = 5.32 \times 10^{-26}\text{ kg}$$

$$\overline{v^2} = 2.33 \times 10^5\ (\text{m/s})^2$$

$$v_{rms} = 483\text{ m/s (about 0.30 mile/s)}$$

The square root of the average of the square of the velocity, v_{rms}, is not the average velocity, but a quantity called the *root mean square velocity*.

(*b*) The pressure of the gas does not matter.

(*c*) The identity of the gas is important, because the mass of the molecule is included in the calculation. (Contrast this conclusion with that of the prior problem.)

13.16. Explain why neon atoms obey the gas laws the same as nitrogen molecules.

Ans. The gas laws work for unbonded atoms as well as for multiatom molecules.

13.17. (*a*) Calculate the square of each of the following numbers: 1, 2, 3, 4, and 5. (*b*) Calculate the average of the numbers. (*c*) Calculate the average of the squares. (*d*) Is the square root of the average of the squares equal to the average of the numbers? (*e*) Explain why quotation marks are used with "average" velocity in the text for the velocity of molecules with average kinetic energies.

Ans. (*a*)

Number	Square
1	1
2	4
3	9
4	16
5	25

(*b*) 3

(*c*) 11

(*d*) The square root of the average of the squares ($\sqrt{11}$) is not equal to the average of the numbers (3).

(*e*) The velocity equal to the square root of the quotient of twice the average kinetic energy divided by the molecular mass, is not really the average velocity. That is, the square root of $\overline{v^2}$ does not give $\overline{v}$, but the root mean square velocity.

13.18. Contrast the motions of the molecules of a sample of gas at rest to those in a hurricane wind.

Ans. At rest, as many molecules are traveling on average in any given direction as in the opposite direction, and at the same average speeds. In a hurricane, the molecules on average are traveling somewhat faster in the direction of the wind than in the opposite direction.

13.19. Oxygen gas and sulfur dioxide gas are at the same temperature. What is the ratio of the "average" velocities of their molecules?

Ans. Since the temperatures are the same, so are the average kinetic energies of their molecules. From Graham's law,

$$\frac{v_1}{v_2} = \sqrt{\frac{MM_2}{MM_1}} = \sqrt{\frac{64.06}{32.00}} = 1.415$$

The oxygen molecules are moving, on average, 1.415 times as fast as the SO_2 molecules.

Solved Problems

INTRODUCTION

14.1. (*a*) What is the formula of a compound of two ions: X^+ and Y^{2-}? (*b*) What is the formula of a covalent compound of two elements: "W" with an oxidation state of +1 and "Z" with an oxidation state of −2?

Ans. We treat the oxidation states in part *b* just like the charges in part *a*. In this manner, we can predict formulas for ionic and covalent compounds. (*a*) X_2Y (b) W_2Z.

ASSIGNING OXIDATION NUMBERS

14.2. Show that rules 2 and 3 (Sec. 14.2) are corollaries of rule 1.

Ans. Rule 2: Uncombined elements have zero charges, and so the oxidation numbers must add up to zero. Since all the atoms are the same, all the oxidation numbers must be the same—0. Rule 3: For monatomic ions, the oxidation numbers of all the atoms add up to the charge on the ion. Since there is only one atom (it is monatomic), the oxidation number of that atom must add up to the charge on the ion; that is, it is equal to the charge on the ion.

14.3. Draw an electron dot diagram for H_2O_2. Assign an oxidation number to oxygen on this basis. Compare this number with that assigned by rule 6 (Sec. 14.2).

Ans.

$$H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$$

Free atom	6
− Controlled	−7
Oxidation number	−1

The electrons shared between the oxygen atoms are counted one for each atom. Peroxide oxygen is assigned an oxidation state of −1 by rule 6 also.

14.4. What is the sum of the oxidation numbers of all the *atoms* in the following compounds or ions? (*a*) PO_4^{3-}, (*b*) VO_2^+, (*c*) ClO_2^-, (*d*) $Cr_2O_7^{2-}$, (*e*) $SiCl_4$, and (*f*) NaCl.

Ans. The sum equals the charge on the species in each case: (*a*) −3 (*b*) +1 (*c*) −1 (*d*) −2 (*e*) 0 (*f*) 0

14.5. Determine the oxidation numbers for the underlined elements: $(\underline{V}O_2)_3\underline{P}O_4$.

Ans. We recognize the phosphate ion, PO_4^{3-}. Each VO_2 ion therefore must have a 1+ charge. The oxidation numbers are +5 for P and +5 for V.

14.6. What is the oxidation number of chlorine in each of the following? (*a*) Cl_2O_3, (*b*) ClO_4^-, and (*c*) ClF_5.

Ans. (*a*) +3 (*b*) +7 (*c*) +5

14.7. Determine the oxidation number for the underlined element: (*a*) $\underline{P}OCl_3$, (*b*) $H\underline{N}O_2$, (*c*) $Na_2\underline{S}O_4$, (*d*) $\underline{P}Cl_5$, and (*e*) $\underline{N}_2O_3$.

Ans. (*a*) +5 (*b*) +3 (*c*) +6 (*d*) +5 (*e*) +3

14.8. Determine the oxidation number for the underlined element: (*a*) $\underline{Cl}O^-$, (*b*) $\underline{P}O_4^{3-}$, (*c*) $\underline{S}O_4^{2-}$, and (*d*) $\underline{V}O^{2+}$.

Ans. (*a*) +1 (*b*) +5 (*c*) +6 (*d*) +4

14.9. What is the oxidation number of Si in $Si_6O_{18}^{12-}$?

Ans.

$$6x + 18(-2) = -12 \qquad x = +4$$

14.10. What oxyacid of nitrogen can be prepared by adding water to N_2O_5? *Hint:* Both compounds have nitrogen in the same oxidation state.

Ans. HNO_3

$$H_2O + N_2O_5 \longrightarrow 2\ HNO_3$$

PERIODIC RELATIONSHIPS OF OXIDATION NUMBERS

14.11. Predict the formulas of two compounds of each of the following pairs of elements: (*a*) S and O, (*b*) Cl and O, (*c*) P and S, (*d*) P and F, (*e*) I and F, and (*f*) S and F.

Ans. The first element in each part is given in its highest oxidation state and in an oxidation state 2 less than the highest. The second element is in its minimum oxidation state. (*a*) SO_3 and SO_2 (*b*) Cl_2O_7 and Cl_2O_5 (*c*) P_2S_5 and P_2S_3 (*d*) PF_5 and PF_3 (*e*) IF_7 and IF_5 (*f*) SF_6 and SF_4

14.12. Predict the formulas of four fluorides of iodine.

Ans. IF_7, IF_5, IF_3 and IF. The oxidation states of iodine in these compounds correspond to the maximum oxidation state for a group VII element and to states 2, 4, and 6 lower. (See Fig. 14-1.)

14.13. Write the formulas for two monatomic ions for each of the following metals: (*a*) Co, (*b*) Tl, (*c*) Sn, and (*d*) Cu.

Ans. (*a*) Co^{3+} and Co^{2+} (the oxidation states of transition metals very in steps of one.) (*b*) Tl^{3+} and Tl^{+} (the maximum oxidation state of a group III element and the state 2 less than the maximum.) (*c*) Sn^{4+} and Sn^{2+} (the maximum oxidation state of a group IV element and the state 2 less than the maximum.) (*d*) Cu^{+} and Cu^{2+} (the maximum oxidation state for the coinage metals is greater than the group number.)

OXIDATION NUMBERS IN INORGANIC NOMENCLATURE

14.14. Name NO_2 and N_2O_4, using the Stock system. Explain why the older system using prefixes is still useful.

Ans. Both compounds have nitrogen in the +4 oxidation state, so if we call NO_2 nitrogen(IV) oxide, what do we call N_2O_4? We actually use the older system for N_2O_4—dinitrogen tetroxide.

BALANCING OXIDATION-REDUCTION EQUATIONS

14.15. Why is it possible to add H^+ and/or H_2O to an equation for a reaction carried out in aqueous acid solution when none visibly appears or disappears?

Ans. The H_2O and H^+ are present in excess in the solution. Therefore, they can react or be produced without the change being noticed.

14.16. How many electrons are involved in a reaction of one atom with a change of oxidation number from (*a*) +2 to −3 and (*b*) +5 to −2?

Ans. (*a*) $2 - (-3) = 5$ 5 electrons are involved (*b*) $5 - (-2) = 7$ 7 electrons are involved

14.17. Identify (*a*) the oxidizing agent, (*b*) the reducing agent, (*c*) the element oxidized, and (*d*) the element reduced in the following reaction:

$$8\ H^+ + CrO_4^{2-} + 3\ Co^{2+} \longrightarrow Cr^{3+} + 3\ Co^{3+} + 4\ H_2O$$

Ans. (*a*) CrO_4^{2-} (*b*) Co^{2+} (*c*) Co (*d*) Cr.
An element in the reducing agent is oxidized; an element in the oxidizing agent is reduced.

14.18. Balance the equation for the reduction of HNO_3 to NH_4NO_3 by Mn by the oxidation number change method. Add other compounds as needed.

Ans.

$$HNO_3 + Mn \longrightarrow NH_4NO_3 + Mn(NO_3)_2$$

The manganese goes up two oxidation numbers, and some of the nitrogen atoms are reduced from +5 to −3:

$$\overbrace{HNO_3 + Mn \longrightarrow NH_4NO_3 + Mn(NO_3)_2}^{(0 \longrightarrow +2) = +2}$$
$$\underbrace{HNO_3 + Mn \longrightarrow NH_4NO_3}_{(+5 \longrightarrow -3) = -8}$$

It takes four Mn atoms per N atom reduced:

$$HNO_3 + 4\ Mn \longrightarrow 1\ NH_4NO_3 + 4\ Mn(NO_3)_2$$

There are other N atoms that were not reduced, but still are present in the nitrate ions. Additional HNO_3 is needed to provide for these.

$$10\ HNO_3 + 4\ Mn \longrightarrow NH_4NO_3 + 4\ Mn(NO_3)_2$$

Water is also produced, needed to balance both the H and O atoms:

$$10\ HNO_3 + 4\ Mn \longrightarrow NH_4NO_3 + 4\ Mn(NO_3)_2 + 3\ H_2O$$

The equation is now balanced, having 10 H atoms, 10 N atoms, 30 O atoms, and 4 Mn atoms on each side.

ELECTROCHEMISTRY

14.19. Even if sodium metal were produced by the electrolysis of aqueous NaCl, what would happen to the sodium produced in the water?

Ans. The sodium is so active that it would react immediately with the water. No elementary sodium should ever be expected from a water solution.

14.20. Explain why Al cannot be produced from its salts in aqueous solution.

Ans. Al is too active; the water will be reduced instead.

14.21. Can a Daniell cell be recharged?

Ans. No. If the Daniell cell were to be recharged, the Cu^{2+} ions would get into the zinc half-cell through the salt bridge. There, they would react directly with the zinc electrode, and the cell would be destroyed.

14.22. Explain why a Daniell cell cannot be placed in a single container, like the lead storage cell.

Ans. The copper(II) ions would migrate to the zinc electrode and be reduced to copper metal directly. The zinc electrode would become copper-plated, and the cell would not function.

14.23. Write a balanced chemical equation for (*a*) the direct reaction of zinc with copper(II) sulfate and (*b*) the overall reaction in a Daniell cell containing $ZnSO_4$ and $CuSO_4$.

Ans. (*a*) and (*b*) $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

14.24. The electrolysis of brine (concentrated NaCl solution) produces hydrogen at the cathode and chlorine at the anode. Write a net ionic equation for each half-reaction and the total reaction. What other chemical is produced in this commercially important process?

Ans.

$$2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$$
$$2\ Cl^- \longrightarrow Cl_2 + 2\ e^-$$
$$2\ Cl^- + 2\ H_2O \longrightarrow Cl_2 + H_2 + 2\ OH^-$$

The other product is NaOH.

14.25. Must two oxidation-reduction half-reactions be carried out (*a*) in the same location and (*b*) at the same time?

Ans. (*a*) No, they may be in different locations, as in electrochemical processes (*b*) Yes. (The electrons cannot appear from nowhere or go nowhere.)

Supplementary Problems

14.26. Explain why we were able to use the charges on the monatomic cations in names in Chap. 6 instead of the required oxidation numbers.

Ans. For monatomic ions, the charge is equal to the oxidation number.

14.27. Determine the oxidation number of oxygen in (*a*) Na_2O_2, (*b*) RbO_2, and (*c*) OF_2.

Ans. (*a*) -1 (*b*) $-\frac{1}{2}$ ($+1 + 2x = 0$, therefore $x = -\frac{1}{2}$) (*c*) $+2$

14.28. Since the reactions in Problem 14.23 are the same, and the Daniell cell produces electric energy, what kind of energy does the direct reaction produce?

Ans. It produces more heat energy than the electrochemical reaction produces.

14.29. Complete and balance the following redox equations:

(*a*) $MnO_4^- + Hg_2^{2+} \longrightarrow Hg^{2+} + Mn^{2+}$

(*b*) $I^- + H_2O_2 \longrightarrow I_2 + H_2O$

(*c*) $Br_2 + OH^- \longrightarrow Br^- + BrO_3^-$

(*d*) $P_4 + OH^- \longrightarrow PH_3 + HPO_3^{2-}$

(*e*) $H_2C_2O_4 + MnO_4^- \longrightarrow Mn^{2+} + CO_2$

(*f*) $Cr(OH)_2 + H_2O_2 \longrightarrow Cr(OH)_3$

Ans. (*a*) $16\,H^+ + 2\,MnO_4^- + 5\,Hg_2^{2+} \longrightarrow 10\,Hg^{2+} + 2\,Mn^{2+} + 8\,H_2O$

(*b*) $2\,H^+ + 2\,I^- + H_2O_2 \longrightarrow I_2 + 2\,H_2O$

(*c*) $3\,Br_2 + 6\,OH^- \longrightarrow 5\,Br^- + BrO_3^- + 3\,H_2O$

(*d*) $2\,H_2O + P_4 + 4\,OH^- \longrightarrow 2\,PH_3 + 2\,HPO_3^{2-}$

(*e*) $6\,H^+ + 5\,H_2C_2O_4 + 2\,MnO_4^- \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$

(*f*) $2\,Cr(OH)_2 + H_2O_2 \longrightarrow 2\,Cr(OH)_3$

14.30. Which of the equations in Problem 14.29 represent reactions in basic solution? How can you tell?

Ans. Reactions (*c*), (*d*), and (*f*) occur in basic solution. The presence of OH^- ions shows immediately that the solution is basic. (The presence of NH_3 also indicates basic solution; in acid solution, this base would react to form NH_4^+.) The other reactions are not in base; H^+ is present. Also, if they were in base, the metal ions would react to form insoluble hydroxides and the simple ions would not be present.

14.31. Complete and balance the following equations:

(*a*) $Zn + H^+ + NO_3^- \longrightarrow NH_4^+ + Zn^{2+}$

(*b*) $Zn + HNO_3 \longrightarrow NH_4NO_3 + Zn(NO_3)_2$

(*c*) How are these equations related? Which is easier to balance?

Ans. (*a*)

$$NO_3^- \longrightarrow NH_4^+ \qquad Zn \longrightarrow Zn^{2+} + 2\,e^-$$
$$8\,e^- + NO_3^- \longrightarrow NH_4^+$$
$$10\,H^+ + 8\,e^- + NO_3^- \longrightarrow NH_4^+$$
$$10\,H^+ + 8\,e^- + NO_3^- \longrightarrow NH_4^+ + 3\,H_2O \qquad 4\,Zn \longrightarrow 4\,Zn^{2+} + 8\,e^-$$

$$10\,H^+ + 4\,Zn + NO_3^- \longrightarrow NH_4^+ + 3\,H_2O + 4\,Zn^{2+}$$

(*b*) Either add 9 NO_3^- to each side of the equation in part *a*:

$$10\,HNO_3 + 4\,Zn \longrightarrow NH_4NO_3 + 3\,H_2O + 4\,Zn(NO_3)_2$$

or

$$2\,HNO_3 \longrightarrow NH_4NO_3 \qquad Zn \longrightarrow Zn(NO_3)_2 + 2\,e^-$$
$$8\,e^- + 2\,HNO_3 \longrightarrow NH_4NO_3 \qquad 2\,HNO_3 + Zn \longrightarrow Zn(NO_3)_2 + 2\,e^-$$
$$8\,H^+ + 8\,e^- + 2\,HNO_3 \longrightarrow NH_4NO_3 \qquad 2\,HNO_3 + Zn \longrightarrow Zn(NO_3)_2 + 2\,e^- + 2\,H^+$$
$$8\,H^+ + 8\,e^- + 2\,HNO_3 \longrightarrow NH_4NO_3 + 3\,H_2O \qquad 8\,HNO_3 + 4\,Zn \longrightarrow 4\,Zn(NO_3)_2 + 8\,e^- + 8\,H^+$$

$$10\,HNO_3 + 4\,Zn \longrightarrow 4\,Zn(NO_3)_2 + NH_4NO_3 + 3\,H_2O$$

(*c*) Part *a* is the net ionic equation for part *b*. It is easier to balance part *a*. To balance part *b*, either amend the balanced net ionic equation of part *a*, or do part *b*, starting from scratch. (There must always be at least one type of ion represented in a balanced half-reaction equation.)

14.32. Balance the following equation by the oxidation number change method:

$$NH_3 + O_2 \longrightarrow NO + H_2O$$

Ans. The O_2 is reduced to the -2 oxidation state; both products contain the reduction product.

$$(-3 \rightarrow +2) = +5$$

$$NH_3 + O_2 \longrightarrow NO + H_2O$$

$$2(0 \rightarrow -2) = -4$$

We know that five O_2 molecules are required, but we still do not know from this calculation how many of the oxygen atoms go to NO or H_2O.

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + H_2O$$

Finish by inspection:

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O$$

14.33. Complete and balance the following equations:

(*a*) $H_2O_2 + Sn^{2+} \longrightarrow Sn^{4+} + H_2O$

(*b*) $Br^- + BrO_3^- \longrightarrow Br_2 + H_2O$

(*c*) $Ce^{4+} + SO_3^{2-} \longrightarrow Ce^{3+} + SO_4^{2-}$

(*d*) $Zn + OH^- \longrightarrow Zn(OH)_4^{2-} + H_2$

(*e*) $Cu_2O + H^+ \longrightarrow Cu + Cu^{2+} + H_2O$

(*f*) $H_2SO_4(\text{conc}) + Zn \longrightarrow H_2S + Zn^{2+}$

(*g*) $HNO_3 + Pb(NO_3)_2 \longrightarrow Pb(NO_3)_4 + NO$

(*h*) $H^+ + NO_3^- + Sn^{2+} \longrightarrow NO + Sn^{4+}$

(*i*) $SO_4^{2-} + I^- + H^+ \longrightarrow SO_2 + I_2 + H_2O$

(*j*) $Cr^{3+} + MnO_4^- \longrightarrow Cr_2O_7^{2-} + Mn^{2+}$

(*k*) $Ag^+ + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + Ag$

Ans. (*a*)

$$+2$$

$$H_2O_2 + Sn^{2+} \longrightarrow Sn^{4+} + 2\,H_2O$$

$$2(-1 \rightarrow -2) = -2$$

$$2\,H^+ + H_2O_2 + Sn^{2+} \longrightarrow Sn^{4+} + 2\,H_2O$$

(*b*) $6\,H^+ + 5\,Br^- + BrO_3^- \longrightarrow 3\,Br_2 + 3\,H_2O$

(*c*)
$$e^- + Ce^{4+} \longrightarrow Ce^{3+}$$
$$H_2O + SO_3^{2-} \longrightarrow SO_4^{2-} + 2\,e^- + 2\,H^+$$
$$\overline{2\,Ce^{4+} + H_2O + SO_3^{2-} \longrightarrow SO_4^{2-} + 2\,H^+ + 2\,Ce^{3+}}$$

(*d*)
$$4\,OH^- + Zn \longrightarrow Zn(OH)_4^{2-} + 2\,e^-$$
$$2\,e^- + 2\,H_2O \longrightarrow 2\,OH^- + H_2$$
$$\overline{2\,H_2O + 2\,OH^- + Zn \longrightarrow Zn(OH)_4^{2-} + H_2}$$

(*e*) $Cu_2O + 2\,H^+ \longrightarrow Cu + Cu^{2+} + H_2O$

Cu^+ is not stable in aqueous solution. Cu(I) is stable in solid compounds like Cu_2O, but when that reacts with an acid, the Cu^+ disproportionates—reacts with itself—to produce a lower and a higher oxidation state.

(*f*)
$$8\,e^- + 8\,H^+ + H_2SO_4 \longrightarrow H_2S + 4\,H_2O$$
$$Zn \longrightarrow Zn^{2+} + 2\,e^-$$
$$\overline{4\,Zn + 8\,H^+ + H_2SO_4 \longrightarrow H_2S + 4\,H_2O + 4\,Zn^{2+}}$$

(g) $(+2 \rightarrow +4) = +2$

$$HNO_3 + Pb(NO_3)_2 \longrightarrow Pb(NO_3)_4 + NO$$

$(+5 \rightarrow +2) = -3$

$$6\,HNO_3 + 2\,HNO_3 + 3\,Pb(NO_3)_2 \longrightarrow 3\,Pb(NO_3)_4 + 2\,NO + 4\,H_2O$$

(for extra nitrate ions)

$$8\,HNO_3 + 3\,Pb(NO_3)_2 \longrightarrow 3\,Pb(NO_3)_4 + 2\,NO + 4\,H_2O$$

(h) $8\,H^+ + 2\,NO_3^- + 3\,Sn^{2+} \longrightarrow 2\,NO + 3\,Sn^{4+} + 4\,H_2O$

(i) $SO_4^{2-} + 2\,I^- + 4\,H^+ \longrightarrow SO_2 + I_2 + 2\,H_2O$

(j) $10\,Cr^{3+} + 6\,MnO_4^- + 11\,H_2O \longrightarrow 5\,Cr_2O_7^{2-} + 6\,Mn^{2+} + 22\,H^+$

(k) $2\,Ag^+ + 2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2\,Ag$

14.34. Consider the following part of an equation:

$$NO_2 + MnO_4^- \longrightarrow Mn^{2+} +$$

(a) If one half-reaction is a reduction, what must the other half-reaction be? (b) To what oxidation state can the nitrogen be changed? (c) Complete and balance the equation.

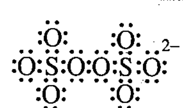
Ans. (a) Since one half-reaction is a reduction, the other half-reacttion must be an oxidation.

(b) The maximum oxidation state for nitrogen is +5, because nitrogen is in periodic group V. Since it starts out in oxidation number +4, it must be oxidized to +5.

(c)
$$NO_2 + MnO_4^- \longrightarrow Mn^{2+} + NO_3^-$$
$$5\,NO_2 + MnO_4^- \longrightarrow Mn^{2+} + 5\,NO_3^-$$
$$H_2O + 5\,NO_2 + MnO_4^- \longrightarrow Mn^{2+} + 5\,NO_3^- + 2\,H^+$$

14.35. What is the oxidation number of sulfur in $S_2O_8^{2-}$, the peroxydisulfate ion?

Ans. If you calculate the oxidation number assuming that the oxygen atoms are normal oxide ions, you get an answer of +7, which is greater than the maximum oxidation number for sulfur. That must mean that one of the pairs of oxygen atoms is a peroxide, and thus the sulfur must be in its highest oxidation number, +6.



14.36. Which of the following reactions (indicated by unbalanced equations) occur in acid solution and which occur in basic solution?

(a) $HNO_3 + Cu \longrightarrow NO + Cu^{2+}$

(b) $CrO_4^{2-} + Fe(OH)_2 \longrightarrow Cr(OH)_3 + Fe(OH)_3$

(c) $N_2H_4 + I^- \longrightarrow NH_4^+ + I_2$

Ans. (a) Acid solution (HNO_3 would not be present in base.) (b) Basic solution (The hydroxides would not be present in acid.) (c) Acid solution (NH_3 rather than NH_4^+ would be present in base.)

14.37. Complete and balance the following equations:

(a) $Cl^- + MnO_2 + H^+ \longrightarrow Mn^{2+} + H_2O + Cl_2$

(b) $ClO^- \longrightarrow Cl^- + ClO_3^-$

(c) $Pb + PbO_2 + SO_4^{2-} \longrightarrow PbSO_4 + H_2O$

(d) $I_3^- + Co(CN)_6^{4-} \longrightarrow Co(CN)_6^{3-} + I^-$

(e) $V^{2+} + H_3AsO_4 \longrightarrow HAsO_2 + VO^{2+}$

(f) $Hg_2^{2+} + CN^- \longrightarrow C_2N_2 + Hg$

(g) $VO^{2+} + AsO_4^{3-} \longrightarrow AsO_2^- + VO_2^+$

Ans. (a) $2\,Cl^- + MnO_2 + 4\,H^+ \longrightarrow Mn^{2+} + 2\,H_2O + Cl_2$

(b) $3\,ClO^- \longrightarrow 2\,Cl^- + ClO_3^-$

(*c*) $4\,H^+ + Pb + PbO_2 + 2\,SO_4{}^{2-} \longrightarrow 2\,PbSO_4 + 2\,H_2O$

(*d*) $I_3{}^- + 2\,Co(CN)_6{}^{4-} \longrightarrow 2\,Co(CN)_6{}^{3-} + 3\,I^-$

(*e*) $V^{2+} + H_3AsO_4 \longrightarrow HAsO_2 + VO^{2+} + H_2O$

(*f*) $Hg_2{}^{2+} + 2\,CN^- \longrightarrow C_2N_2 + 2\,Hg$

(*g*) $2\,VO^{2+} + AsO_4{}^{3-} \longrightarrow AsO_2{}^- + 2\,VO_2{}^+$

14.38. The oxidizing ability of H_2SO_4 depends on its concentration. Which element is reduced by reaction of Zn on H_2SO_4 in each of the following reactions?

$$Zn + H_2SO_4(\text{dilute}) \longrightarrow ZnSO_4 + H_2$$

$$4\,Zn + 5\,H_2SO_4(\text{conc}) \longrightarrow H_2S + 4\,H_2O + 4\,ZnSO_4$$

Ans. In the first reaction, hydrogen is reduced. In the second reaction, sulfur is reduced.

14.39. Complete and balance the following equation:

$$Sb_2S_3 + HNO_3 \longrightarrow H_3SbO_4 + SO_2 + NO$$

Ans. $$3\,Sb_2S_3 + 22\,HNO_3 \longrightarrow 6\,H_3SbO_4 + 9\,SO_2 + 22\,NO + 2\,H_2O$$

14.40. What is the maximum oxidation state of fluorine in any compound?

Ans. The only oxidation state of fluorine in a compound is -1; it is the most electronegative element. (It always has control of both shared electrons, except in the element F_2.)

14.41. Calculate the oxidation number of carbon in (*a*) CH_2O and (*b*) CH_2F_2.

Ans. (*a*) 0 (*b*) 0

14.42. What is the more likely formula for bismuth in the +5 oxidation state—Bi^{5+} or $BiO_3{}^-$?

Ans. $BiO_3{}^-$. There are no 5+ monatomic ions.

14.43. Explain why direct current (dc) rather than alternating current (ac) is used for electrolysis. Why is direct current used in cars?

Ans. In direct current, the electrons flow in the same direction all the time. In alternating current, the electrons flow one way for a short period of time (typically $\frac{1}{60}$ s), and then they flow the other way. To get any electrolysis that is not immediately undone, direct current is required. Direct current is also used in cars because cells generate direct current.