Chapter 1

The Nature and Conceptual Basis of Chemistry

1.2 "Absolute" means pure, so absolute alcohol is a substance; milk is a mixture; copper wire is a substance. Rust is a mixture (the reason for this last answer is discussed on page 7 of the text in the context of salt versus sodium chloride). Barium bromide is a substance. Concrete, baking soda, and baking powder are all mixtures.

Absolute alcohol and barium bromide are compounds; copper wire is an element. All of the mixtures are heterogeneous.

1.4 Proving that a material is *not* an element involves finding one of the many possible ways of breaking it down into simpler substances. To prove that a material *is* an element requires showing that there is no way to decompose it. It is always possible that trying a new method will convert it into simpler substances.

1.6 The ratio of the mass of tellurium to the mass of hafnium in this compound is

$$\frac{\text{mass Te}}{\text{mass Hf}} = \frac{31.5\text{ g Te}}{25.0\text{ g Hf}} = 1.26\frac{\text{g Te}}{\text{g Hf}}$$

Because the compound from the rock is identical, it contains Te and Hf in the same ratio.

$$\text{mass Te} = 0.125\text{ g Hf} \times \left(1.26\frac{\text{g Te}}{\text{g Hf}}\right) = 0.158\text{ g Te}$$

The compound may of course contain any number of other elements.

1.8 (a) In each case the mass of fluorine that combines with 1.0000 g of iodine is simply the mass percentage of fluorine divided by the mass percentage of iodine. This is best proved by considering samples of the compounds that have masses of 100.000 g. The masses contributed by each element in the compounds are then very easily computed. The ratios in the last column of the following table, which are formed by the indicated divisions, are the answers.

Compound 1	13.021 g F/86.979 g I	0.14970 g F/ g I
Compound 2	30.993 g F/69.007 g I	0.44913 g F/ g I
Compound 3	42.809 g F/57.191 g I	0.74853 g F/ g I
Compound 4	51.171 g F/48.829 g I	1.04796 g F/ g I

(b) The law of multiple proportions involves the ratio of these ratios. Simply divide all four of the answers in part (a) by the smallest of the answers. The results are: 1.0000 for compound 1; 3.0002 for compound 2; 5.0002 for compound 3; 7.0004 for compound 4. These equal the small whole numbers 1, 3, 5, and 7 within the precision of the data.

1.10 As in problem 1.8, we calculate the masses of chlorine per gram of tungsten in the four compounds. These are

Compound 1	27.83 g Cl/72.17 g W	0.3856 g Cl/ g W
Compound 2	43.55 g Cl/56.45 g W	0.7715 g Cl/ g W
Compound 3	49.09 g Cl/50.91 g W	0.9643 g Cl/ g W
Compound 4	53.64 g Cl/46.36 g W	1.1570 g Cl/ g W

The ratios of each mass of chlorine to the smallest one are

$$0.7715/0.3856 = 2.0008 = 4:2$$
$$0.9643/0.3856 = 2.5008 = 5:2$$
$$1.1570/0.3856 = 3.0005 = 6:2$$

One possible set of formulas is WCl_2, WCl_4, WCl_5, and WCl_6. The same result is confirmed by using a table of relative atomic masses.

1.12 The *only* products are gaseous N_2 and gaseous H_2. From the formula of the starting compound there are twice as many molecules of H_2 as of N_2 in the products. The law of combining volumes (or, in this case, the law of "uncombining" volumes) then assures that the volume of hydrogen is twice the volume of nitrogen as long as the temperature and pressure remain unchanged. The answer is 27.4 mL.

1.14 The balanced chemical equation for this reaction is

$$2\,CH_3OH + 3\,O_2 \rightarrow 2\,CO_2 + 4\,H_2O$$

2.0 L of CO_2 and 4.0 L of H_2O are produced from 2.0 L of CH_3OH, according to the law of combining volumes.

1.16 (a) Promethium has an atomic number of 61; the ratio of the number of neutrons to protons in ^{145}Pm is $(145 - 61)/61 = 1.377$.

(b) A neutral atom of Pm has 61 electrons.

1.18 The $^{266}_{109}$Mt atom has 109 protons, 109 electrons, and 157 neutrons.

1.20 The atomic mass of naturally occurring neon is found by multiplying the isotope fractional abundances by their masses and adding

$$(0.9000 \times 19.99212) + (0.0027 \times 20.99316) + (0.0973 \times 21.99132) = 20.19$$

1.22 This problem resembles problem 1-20, except that the relative mass of one of the five isotopes of Zr is not known, and the relative atomic mass of natural zirconium (91.224) is known. The natural abundance of the isotope of interest is known by difference

$$1 - 0.1127 - 0.1717 - 0.1733 - 0.0278 = 0.5145$$

Let the relative mass of this isotope be x. Then

$$91.224 = 0.5145x + 0.1127(90.9056) + 0.1717(91.9050) + 0.1733(93.9063) + 0.0278(95.9083)$$
$$x = 89.91$$

1.24 The 100 million atoms of fluorine will weigh 18.998403/12.00000 times the mass of 100 million atoms of ^{12}C. Avogadro's number of ^{12}C atoms weighs exactly 12 g, so 100 million atoms of ^{12}C weighs

$$12.00000 \text{ g} \times \left(\frac{100,000,000}{6.022142 \times 10^{23}}\right) = 1.992646 \times 10^{-15} \text{ g}$$

The mass of the fluorine is 3.154758×10^{-15} g.

1.26 The point of the problem is to assure that students properly handle the nesting of parentheses in chemical formulas when they compute molecular masses and molar masses. The answers: (a) 177.382; (b) 598.156; (c) 254.2; (d) 98.079; (e) 450.446. There are no units in these answers because they are relative masses.

1.28 There are Avogadro's number of gold atoms in a mole of gold, each with a diameter of 2.88×10^{-10} m. The length of the line is $(6.022 \times 10^{23})(2.88 \times 10^{-10} \text{ m}) = 1.734 \times 10^{14}$ m. This is over 1100 times the distance from the earth to the sun.

1.30 Before we can arrange the four samples by mass, we must express the amounts of each in the same unit of mass. In the case of the SF_4, we convert from the given number of moles to grams using the molar mass. In the cases of the Cl_2O_7 and Ar, a preliminary conversion from the given number of particles to chemical amount is necessary; the amount of CH_4 is already in grams. The results are:

$$SF_4 \text{ (115 g)} < CH_4 \text{ (117 g)} < Cl_2O_7 \text{ (264 g)} < Ar \text{ (2770 g)}$$

1.32

$$10.0 \text{ cm}^3 \text{ Au} \times \left(\frac{19.32 \text{ g Au}}{1 \text{ cm}^3 \text{ Au}}\right) \times \left(\frac{1 \text{ troy ounce}}{31.1035 \text{ g Au}}\right) \times \left(\frac{\$400}{1 \text{ troy ounce}}\right) = \$2.4846 \times 10^3$$

The cost to three significant figures is \$2480.

1.34 Under these conditions, 415 cm^3 contains

$$(415 \text{ cm}^3)(0.00278 \text{ g cm}^{-3}) = 1.1537 \text{ g} = 0.0185 \text{ mol } Si_2H_6$$

The number of molecules is Avogadro's number times this, which is

$$(0.0185 \text{ mol})(6.022 \times 10^{23} \text{ molecules mol}^{-1}) = 1.117 \times 10^{22} \text{ molecules}$$

Because each molecule of Si_2H_6 contains two Si atoms,

$$\text{atoms Si} = 2 \times 1.117 \times 10^{22} = 2.23 \times 10^{22} \text{ atoms Si}$$

1.36 Let us first convert the speed to SI units:

$$\left(95\frac{\text{miles}}{\text{h}}\right)\left(\frac{5280 \text{ ft}}{1 \text{ mile}}\right)\left(\frac{0.3048 \text{ m}}{1 \text{ ft}}\right)\left(\frac{1 \text{ h}}{3600 \text{ s}}\right) = 42.5 \text{ m s}^{-1}$$

The work done on the ball is equal to its change in kinetic energy, $\frac{1}{2}mv^2 - 0 = \frac{1}{2}mv^2$.

$$\begin{aligned}\text{work} &= \frac{1}{2}mv^2 = \frac{1}{2}(0.145 \text{ kg})(42.5 \text{ m s}^{-1})^2 \\ &= 131 \text{ kg m}^2 \text{ s}^{-2} = 1.3 \times 10^2 \text{ J}\end{aligned}$$

1.38 (a) As suggested in the hint, a good approach to this problem is to look at *differences* in charge. So, ranking the droplets from least to most charge, we also note the amount by which the charge differs from the charge on the previous droplet in the list.

Drop	Charge/10^{-19} C	Difference/10^{-19} C	Charge/1.64×10^{-19} C
1	6.563	—	4.00
2	8.204	1.641	5.00
3	11.50	3.296	7.01
4	13.13	1.63	8.01
5	16.48	3.35	10.0
6	18.08	1.60	11.0
7	19.71	1.63	12.0
8	22.89	3.28	14.0
9	26.18	3.29	16.0

The data all differ from the adjacent values in the list by either 1.64×10^{-19} C or twice that value. This suggests that there is a fundamental unit of charge that is approximately equal to 1.64×10^{-19} C. Dividing this quantity into the observed charges gives the number of electrons on each droplet.

(b) If we divide each observed charge by the integral charge the droplet seems to have, we get these values for the electron charge:

$$\begin{array}{ccc}
1.6407 \times 10^{-19}\ \mathrm{C} & 1.640 \times 10^{-19}\ \mathrm{C} & 1.6425 \times 10^{-19}\ \mathrm{C} \\
1.6408 \times 10^{-19}\ \mathrm{C} & 1.648 \times 10^{-19}\ \mathrm{C} & 1.635 \times 10^{-19}\ \mathrm{C} \\
1.643 \times 10^{-19}\ \mathrm{C} & 1.6436 \times 10^{-19}\ \mathrm{C} & 1.636 \times 10^{-19}\ \mathrm{C}
\end{array}$$

The average of all these values is 1.641×10^{-19} C.

(c) We have chosen the least possible charge to fit the data. The data could be any fraction (1/2, 1/3, 1/4, etc.) of the value suggested. One could only check the result by a thorough search for droplets with fractional charge.

1.40

$$\text{Density of neutron star} = \frac{\text{mass}}{\text{volume}} = \frac{6.0 \times 10^{56} \times 1.675 \times 10^{-24}\ \mathrm{g}}{(4/3)\pi(20 \times 10^{5}\ \mathrm{cm})^3} = 3.0 \times 10^{13}\ \mathrm{g\ cm^{-3}}$$

$$\text{Mass of } {}^{232}\text{Th nucleus} = 142(1.675 \times 10^{-24}\ \mathrm{kg}) + 90(1.673 \times 10^{-24}\ \mathrm{g}) = 3.884 \times 10^{-22}\ \mathrm{g}$$

$$\text{Density of } {}^{232}\text{Th nucleus} = \frac{3.884 \times 10^{-22}\ \mathrm{g}}{(4/3)\pi(9.1 \times 10^{-13}\ \mathrm{cm})^3} = 1.2 \times 10^{14}\ \mathrm{g\ cm^{-3}}$$

This is four times larger than the density of a neutron star.

1.42 Let x be the *fractional* abundance of ^{85}Rb and $1 - x$ be the abundance of ^{87}Rb. Then

$$\begin{gathered}
x(84.9117) + (1 - x)(86.9092) = 85.4678 \\
1.4414 = 1.9975x \\
x = 0.7216
\end{gathered}$$

The percentage of ^{85}Rb is 72.16%; ^{87}Rb is 27.84%.

1.44

$$m_{\text{ball}} = (2.0\ \text{oz})\left(\frac{1\ \text{lb}}{16\ \text{oz}}\right)\left(\frac{0.4536\ \text{kg}}{1\ \text{lb}}\right) = 0.057\ \text{kg}$$

$$v_{\text{ball}} = \left(98\frac{\text{miles}}{\text{h}}\right)\left(\frac{5280\ \text{ft}}{1\ \text{mile}}\right)\left(\frac{0.3048\ \text{m}}{1\ \text{ft}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right) = 43.8\ \text{m s}^{-1}$$

$$\text{Kinetic energy} = \frac{1}{2}mv^2 = \frac{1}{2}(0.057\ \text{kg})(43.8\ \text{m s}^{-1})^2 = 55\ \text{J}$$

No work is done on the building because the wall is not displaced.

Chapter 2

Chemical Formulas, Chemical Equations, and Reaction Yields

2.2 The molar mass of acetaminophen, $C_8H_9NO_2$, is 151.165 g mol^{-1}. The percentages are found by dividing this into the mass of each element in one mole of compound, and multiplying by 100%

$$\%\text{C} \quad \frac{8 \times 12.011 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} \times 100\% = 63.56\% \text{ C}$$

$$\%\text{H} \quad \frac{9 \times 1.00794 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} \times 100\% = 6.001\% \text{ H}$$

$$\%\text{N} \quad \frac{1 \times 14.0067 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} \times 100\% = 9.266\% \text{ N}$$

$$\%\text{O} \quad \frac{2 \times 15.9994 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} \times 100\% = 21.17\% \text{ O}$$

2.4 The mass percentage of fluorine in each of the compounds can certainly be calculated and the resulting numbers used to get the required order. It saves work however to *estimate* the fluorine content of each compound. Thus, HF is certainly the richest possible compound in fluorine by mass because the only other atom is the very light hydrogen atom—there is only 1 unit of non-fluorine mass per fluorine atom. The non-fluorine mass per fluorine atom in C_6HF_5 is about $(6 \times 12)/5 \approx 14$; in BrF it is 79.9; in UF_6 it is $238/6 \approx 40$. The desired order is therefore $\text{BrF} < UF_6 < C_6HF_5 < \text{HF}$.

2.6 The pharmacist mixes 286 g of one compound with 150 g of another, using water as a mixing agent. After all the water is driven away, the mixture obviously weighs 436 g. The first compound (Na_2CO_3) contains a fixed proportion of carbon as does the second ($C_2H_5NO_2$). The mass of carbon in the Na_2CO_3 is $(12.011/105.989) \times 286$ g and the mass of carbon in the $C_2H_5NO_2$ is $(2 \times 12.011/75.067) \times 150$ g where the 105.989 and 75.067 are the respective molecular masses of the compounds. The mass of carbon in the mixture is the sum of these two masses. It equals 80.411 g. The mass percentage of carbon is this mass divided by 436 g and multiplied by 100%. It is 18.4%.

2.8 Imagine a sample of bromoform of arbitrary mass, say 100.0 g. The mass of bromine in this sample is 94.85 g, the mass of hydrogen is 0.40 g, and the mass of carbon is 4.75 g. Convert each of these masses to chemical amount by dividing by the molar mass of the element: there are 1.19445 mol of Br, 0.39685 mol of H, and 0.39547 mol of C. (Nonsignificant figures appear in these intermediate values for the sake of greater precision in the final result.) The three chemical amounts stand in the ratio of 3.02 to 1.003 to 1. Within the precision of the data this ratio is 3 to 1 to 1. The empirical formula is Br_3HC.

2.10 In 100.0000 g of the compound there is 1.6907 g of O and 98.3093 g of Cs. The chemical amount of oxygen in the 100.00 g of compound is its mass divided by its molar mass; it equals 0.10567 mol. The chemical amount of cesium is 0.73969 mol. The ratio of the chemical amounts is 7.000 to 1, making the empirical formula Cs_7O.

2.12 The empirical formulas of the five compounds are

Compound	Formula
A	CO_2
B	CO
C	C_4O_3
D	C_3O_2
E	C_5O_2

All five of these compositions exist. The first two are commonplace. The third is mellitic anhydride and has the molecular formula $C_{12}O_9$. The last two have molecular formulas identical to their empirical formulas and are "suboxides" of carbon.

2.14 (a)

$$\text{moles Ca} = \text{moles CaO} = \frac{2.389\text{ g}}{56.0774\text{ g mol}^{-1}} = 0.04260\ \text{mol}$$

$$\text{moles C} = \text{moles CO}_2 = \frac{1.876\text{ g}}{44.010\text{ g mol}^{-1}} = 0.04263\ \text{mol}$$

$$\text{moles N} = \text{moles NO}_2 = \frac{3.921\text{ g}}{46.0055\text{ g mol}^{-1}} = 0.08523\text{ mol}$$

$$\frac{\text{mol N}}{\text{mol Ca}} = \frac{0.08523}{0.04260} = 2.001 \approx 2$$

The empirical formula is $CaCN_2$.

2.16 Because a given volume contains the same number of molecules, the ratio of molecular masses equals the ratio of densities:

$$\frac{\text{molecular mass of P}_n}{\text{molecular mass of N}_2} = \frac{2.7\text{ g L}^{-1}}{0.62\text{ g L}^{-1}}$$

$$\text{molecular mass of P}_n = \left(\frac{2.7}{0.62}\right)(28.014) = 122$$

Because the atomic mass of P is 30.97, n must be

$$n = \frac{122}{30.97} = 3.94 \approx 4$$

There are four P atoms per molecule under these conditions.

2.18 (a) Molecular mass $= (2.53)(28.013) = 70.9$

(b) $$\frac{8.21\ \text{g}}{70.9\ \text{g mol}^{-1}} = 0.1158\ \text{mol compound}$$

$$\frac{1.62\ \text{g}}{14.007\ \text{g mol}^{-1}} = 0.1157\ \text{mol N atoms}$$

Each molecule has one N atom

(c) $70.9 - 14.0 = 56.9$

(d) $\frac{56.9}{2} = 28.5$, $\frac{56.9}{3} = 19.0$, $\frac{56.9}{4} = 14.2$, and so forth. Best choice is F (atomic mass 19.0).

(e) NF_3

2.20 (a) $2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2$
(b) $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$
(c) $2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe(OH)_2$
(d) $2\ HSbCl_4 + 3\ H_2S \rightarrow Sb_2S_3 + 8\ HCl$
(e) $2\ Al + Cr_2O_3 \rightarrow Al_2O_3 + 2\ Cr$
(f) $XeF_4 + 2\ H_2O \rightarrow Xe + O_2 + 4\ HF$
(g) $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4\ H_2O$
(h) $NaBH_4 + 2\ H_2O \rightarrow NaBO_2 + 4\ H_2$

2.22 (a)

$$\left(\frac{1.000\ \text{g CaCO}_3}{100.09\ \text{g mol}^{-1}}\right)\left(\frac{1\ \text{mol Ca(OH)}_2}{1\ \text{mol CaCO}_3}\right) \times 74.094\ \text{g mol}^{-1} = 0.7403\ \text{g Ca(OH)}_2$$

(b)

$$\left(\frac{1.000\ \text{g C}_3\text{H}_8}{44.096\ \text{g mol}^{-1}}\right)\left(\frac{3\ \text{mol CO}_2}{1\ \text{mol C}_3\text{H}_8}\right) \times 44.010\ \text{g mol}^{-1} = 2.994\ \text{g CO}_2$$

(c)

$$\left(\frac{1.000\ \text{g MgNH}_4\text{PO}_4}{137.315\ \text{g mol}^{-1}}\right)\left(\frac{1\ \text{mol Mg}_2\text{P}_2\text{O}_7}{2\ \text{mol MgNH}_4\text{PO}_4}\right) \times 222.55\ \text{g mol}^{-1} = 0.8104\ \text{g Mg}_2\text{P}_2\text{O}_7$$

2.24 **Whatever the reaction or series of reactions that gives $Pt_2C_{10}H_{18}N_2S_2O_6$, the chemical amount that forms cannot exceed half the chemical amount of platinum because the compound contains two Pt per molecule. Thus:**

$$1.406\ \text{g Pt} \times \left(\frac{1\ \text{mol Pt}}{195.08\ \text{g Pt}}\right) \times \left(\frac{1\ \text{mol Pt}_2\text{C}_{10}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_6}{2\ \text{mol Pt}}\right)$$
$$\times \left(\frac{716.55\ \text{g Pt}_2\text{C}_{10}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_6}{1\ \text{mol Pt}_2\text{C}_{10}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_6}\right) = 2.582\ \text{g Pt}_2\text{C}_{10}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_6$$

2.26 Use the equation $Si_4H_{10} + 13/2\ O_2 \rightarrow 4\ SiO_2 + 5\ H_2O$:

$$m_{SiO_2} = (25.0\ \text{cm}^3\ \text{Si}_4\text{H}_{10}) \times \left(\frac{1\ \text{g}}{0.825\ \text{cm}^3}\right) \times \left(\frac{1\ \text{mol}}{122.42\ \text{g}}\right)$$
$$\times \left(\frac{4\ \text{mol SiO}_2}{1\ \text{mol Si}_4\text{H}_{10}}\right) \times \left(\frac{60.0843\ \text{g SiO}_2}{1\ \text{mol SiO}_2}\right) = 40.5\ \text{g}$$

2.28

$$67.2 \text{ g S} \times \left(\frac{1 \text{ mol S}}{32.066 \text{ g S}}\right) \times \left(\frac{1 \text{ mol CS}_2}{4 \text{ mol S}}\right) \times \left(\frac{76.143 \text{ g CS}_2}{1 \text{ mol CS}_2}\right) = 39.9 \text{ g CS}_2$$

2.30

$$\frac{69.8 \text{ g P}_4}{123.895 \text{ g mol}^{-1}} = 0.5634 \text{ mol P}_4$$

$$(0.5634 \text{ mol P}_4)\left(\frac{2 \text{ mol Ca}_3(\text{PO}_4)_2}{1 \text{ mol P}_4}\right) = 1.1268 \text{ mol Ca}_3(\text{PO}_4)_2$$

$$(1.1268 \text{ mol})(310.18 \text{ g mol}^{-1}) = 349 \text{ g Ca}_3(\text{PO}_4)_2$$

$$(0.5634 \text{ mol P}_4)\left(\frac{6 \text{ mol CaSiO}_3}{1 \text{ mol P}_4}\right) = 3.380 \text{ mol CaSiO}_3$$

$$(3.380 \text{ mol})(116.16 \text{ g mol}^{-1}) = 393 \text{ g CaSiO}_3$$

2.32 (a) Let $\mathcal{M}$ be the molar mass of A. Then $\mathcal{M} + 3(126.90)$ is the molar mass of $\mathrm{AI_3}$.

$$n_{\mathrm{AI_3}} = \frac{0.8000 \text{ g}}{\mathcal{M} + 3(126.90) \text{ g mol}^{-1}} = n_{\mathrm{ACl_3}}$$

$$m_{\mathrm{ACl_3}} = \frac{0.8000 \text{ g}}{\mathcal{M} + 3(126.90) \text{ g mol}^{-1}} \times (\mathcal{M} + 3(35.453) \text{ g mol}^{-1}) = 0.3776 \text{ g}$$

$$0.8000[\mathcal{M} + 106.36] = 0.3776[\mathcal{M} + 380.7]$$

Solving for $\mathcal{M}$ gives $\mathcal{M} = 138.9 \text{ g mol}^{-1}$

(b) The element is lanthanum, La.

2.34

$$\frac{0.738 \text{ g}}{2.016 \text{ g mol}^{-1}} = 0.366 \text{ mol H}_2$$

Suppose the mass of iron originally was x g. Then

$$\text{moles Fe} = \frac{x \text{ g Fe}}{55.847 \text{ g mol}^{-1}} \quad \text{and} \quad \text{moles Al} = \frac{(9.62 - x) \text{ g Al}}{26.982 \text{ g mol}^{-1}}$$

Hydrogen (0.366 mol) is produced by the reaction of Fe and Al. Adding the two contributions gives

$$\frac{x \text{ g Fe}}{55.847 \text{ g mol}^{-1}}\left(\frac{1 \text{ mol H}_2}{1 \text{ mol Fe}}\right) + \frac{(9.62 - x) \text{ g Al}}{26.982 \text{ g mol}^{-1}}\left(\frac{3 \text{ mol H}_2}{2 \text{ mol Al}}\right) = 0.366 \text{ mol H}_2$$

$$-0.03769x + 0.5348 = 0.366$$

$$x = 4.48 \text{ g Fe}$$

2.36 (a) $\mathrm{NH_3 + CH_4 \rightarrow HCN + 3\ H_2}$

(b)

$$\frac{500.0 \text{ g CH}_4}{16.043 \text{ g mol}^{-1}} = 31.17 \text{ mol CH}_4 \quad \text{and} \quad \frac{200.0 \text{ g NH}_3}{17.031 \text{ g mol}^{-1}} = 11.74 \text{ mol NH}_3$$

NH_3 is the limiting reactant. After the reaction there will be

$$11.74 \text{ mol } NH_3 \left(\frac{1 \text{ mol HCN}}{1 \text{ mol } NH_3}\right) \times 27.026 \text{ g mol}^{-1} = 317.3 \text{ g HCN}$$

$$11.74 \text{ mol } NH_3 \left(\frac{3 \text{ mol } H_2}{1 \text{ mol } NH_3}\right) \times 2.0158 \text{ g mol}^{-1} = 71.0 \text{ g } H_2$$

$$(31.17 - 11.74 \text{ mol } CH_4)(16.043 \text{ g mol}^{-1}) = 311.7 \text{ g } CH_4$$

2.38 The theoretical yield of $TiCl_4$ is

$$\left(\frac{7390 \text{ g } TiO_2}{79.88 \text{ g mol}^{-1}}\right) \times \left(\frac{1 \text{ mol } TiCl_4}{1 \text{ mol } TiO_2}\right) \times (189.69 \text{ g mol}^{-1}) = 1.755 \times 10^4 \text{ g} = 17.55 \text{ kg } TiCl_4$$

The percentage yield is

$$\left(\frac{14.24 \text{ kg}}{17.55 \text{ kg}}\right) \times 100\% = 81.1\%$$

2.40 The mass percentages in the two oxides are given to six significant figures; we carry out the calculation to equally high precision. There is 0.43132 mol of W in a 100.000 g sample of the white oxide, and 1.29395 mol of O in the same sample. The ratio of these chemical amounts is 3.0000—the empirical formula is WO_3. In the blue oxide the chemical amounts in a 100.000 g sample are 0.43975 mol W and 1.19709 mol of O. The ratio of these two is 2.72223. This turns out to equal the ratio of 49 to 18, within the precision of the data. Hence the formula $W_{18}O_{49}$ is a correct answer. The blue oxide is really a nonstoichiometric compound, however.

2.42 Consider a 100.00-g sample of this binary compound. It contains 78.06 g of Ni and 21.94 g of O. This is 78.06 g/58.69 g mol^{-1} = 1.330 mol of Ni and 21.94 g/15.9994 g mol^{-1} = 1.371 mol of O. The ratio of these two chemical amounts is 1.031 to 1. If the data are truly precise to four significant figures, the compound is almost certainly a nonstoichiometric compound. The "almost" appears because "$Ni_{1000}O_{1031}$" is a conceivable stoichiometric formulation. These subscript are whole numbers, but they are hardly small whole numbers.

2.44

$$\text{Chemical amount of B} = \frac{0.664 \text{ g B}}{10.811 \text{ g mol}^{-1}} = 0.0614 \text{ mol B}$$

Mass of Cl in original compound = 2.842 g − 0.664 g = 2.178 g Cl

$$\text{Chemical amount of Cl} = \frac{2.178 \text{ g Cl}}{35.453 \text{ g mol}^{-1}} = 0.0614 \text{ mol Cl}$$

$$\frac{0.0614 \text{ mol B}}{0.0614 \text{ mol Cl}} = \frac{1 \text{ mol B}}{1 \text{ mol Cl}} \text{ so the empirical formula is BCl}$$

$$\text{Chemical amount of } Cl_2 \text{ produced} = \left(\frac{1 \text{ mol } Cl_2}{2 \text{ mol Cl}}\right) \times (0.0614 \text{ mol Cl})$$

$$= 0.0307 \text{ mol } Cl_2$$

From Avogadro's hypothesis, the chemical amount of compound in the original 0.153 L must be

$$\left(\frac{0.153 \text{ L compound}}{0.688 \text{ L } Cl_2}\right) \times 0.0307 \text{ mol } Cl_2 = 0.00683 \text{ mol compound}$$

Its approximate molar mass is

$$\frac{2.842 \text{ g}}{0.00683 \text{ mol}} = 416.3 \text{ g mol}^{-1}$$

The molar mass of the empirical formula, BCl, is 46.264 g mol^{-1}. $\frac{416.3}{46.264} = 9.00$, so the molecular formula must be B_9Cl_9.

2.46 The balanced chemical equation reads

$$C_{14}H_{18}N_2O_5 + 2\ H_2O \rightarrow C_4H_7NO_4 + CH_3OH + \text{phenylalanine}$$

By balancing the chemical amounts of C, H, N and O on both sides, we determine the molecular formula of phenylalanine to be $C_9H_{12}NO_2$.

2.48 If we assume that all the carbon is evolved as CH_4, then 1 mol Al_4C_3 generates 3 mol CH_4

$$\text{moles } CH_4 = \left(\frac{63.2 \text{ g } Al_4C_3}{143.96 \text{ g mol}^{-1}}\right)\left(\frac{3 \text{ mol } CH_4}{1 \text{ mol } Al_4C_3}\right) = 1.317 \text{ mol}$$

$$(1.317 \text{ mol})(16.043 \text{ g mol}^{-1}) = 21.1 \text{ g}$$

2.50

$$\frac{0.211 \text{ g } CO_2}{44.010 \text{ g mol}^{-1}} = 0.004794 \text{ mol } CO_2$$

Let x = mass of $SrCO_3$; $0.800 - x$ = mass of $BaCO_3$.

$$\text{moles } SrCO_3 = \frac{x \text{ g}}{147.63 \text{ g mol}^{-1}} \quad \text{and} \quad \text{moles } BaCO_3 = \frac{0.800 - x \text{ g}}{197.34 \text{ g mol}^{-1}}$$

Because each mole of $SrCO_3$ and $BaCO_3$ gives one mole of CO_2,

$$\frac{x}{147.63} + \frac{0.800 - x}{197.34} = 0.004794$$

$$x \doteq 0.434 \text{ g } SrCO_3$$

$$\% \ SrCO_3 = \frac{0.434}{0.800} \times 100\% = 54.2\%$$

2.52 Suppose your gas mileage is 20 miles per gallon. Then reducing driving by 20 miles per week would save 1 gallon per week, or 52 gallons per year. Converted to the metric system this is

$$52 \text{ gallons} \times \left(\frac{3.785 \text{ L}}{1 \text{ gallon}}\right) = 200 \text{ L gasoline}$$

Take the density of gasoline to be that of water, which is 1 g cm^{-3}, or 1 kg L^{-1}. This is then 200 kg of gasoline. Using the chemical formula C_8H_{18}, it is

$$\frac{200 \times 10^3 \text{ g } C_8H_{18}}{114.2 \text{ g mol}^{-1}} = 1.75 \times 10^3 \text{ mol } C_8H_{18}$$

Because 1 mol C_8H_{18} generates 8 mol CO_2, the chemical amount of CO_2 produced is 8 times this, or 1.4×10^4 mol CO_2. Its mass is

$$(1.4 \times 10^4 \text{ mol}) \times (44 \text{ g mol}^{-1}) = 6.2 \times 10^5 \text{ g} = 620 \text{ kg}$$

Converting this to pounds gives

$$620\ \text{kg}\left(\frac{1\ \text{pound}}{0.4536\ \text{kg}}\right) = 1400\ \text{pounds}$$

This is on the order of 1000 pounds, consistent with the statement in the problem.

2.54 The theoretical yield of the $KClO_4$ must be computed and then compared to the observed yield of 3.00 g. First we balance the chemical equation:

$$4\ KClO_3(s) \rightarrow 3\ KClO_4(s) + KCl(s)$$

$$m_{KClO_4} = 4.00\ \text{g}\ KClO_3 \times \left(\frac{1\ \text{mol}\ KClO_3}{122.549\ \text{g}\ KClO_3}\right) \times \left(\frac{3\ \text{mol}\ KClO_4}{4\ \text{mol}\ KClO_3}\right) \times \left(\frac{138.549\ \text{g}\ KClO_4}{1\ \text{mol}\ KClO_4}\right) = 3.392\ \text{g}\ KClO_4$$

The comparison is performed by dividing the actual by the theoretical yield and multiplying by 100%. The result is 88.5%.

2.56 The yield of the product is less than the theoretical, and this fact must be reckoned with. A very good way is to use the percentage yield to construct an additional unit-factor (the second factor in the following):

$$m_{Si} = 125\ \text{g}\ Si_3N_4\ \text{isolated} \times \left(\frac{100\ \text{g}\ Si_3N_4\ \text{formed}}{95.0\ \text{g}\ Si_3N_4\ \text{isolated}}\right) \times \left(\frac{1\ \text{mol}\ Si_3N_4}{148.286\ \text{g}\ Si_3N_4\ \text{formed}}\right) \times \left(\frac{3\ \text{mol Si}}{1\ \text{mol}\ Si_3N_4}\right) \times \left(\frac{28.086\ \text{g Si}}{1\ \text{mol Si}}\right) = 74.8\ \text{g Si}$$

Chapter 3

Chemical Bonding: The Classical Description

3.2 In the following the melting points (top line), boiling points (middle line), and densities (bottom line) of the four immediate neighbors of technetium are arrayed as in the periodic table.

	1244 1962 7.2	
2610 5560 10.2	Tc	2310 3900 12.3
	3180 5627 20.5	

We have no reason to treat trends across the table as any more or less strong than trends down the table. Hence, we just average the four melting points to get a predicted melting point, and do the same with the boiling points and the densities to get a predicted boiling point and density. The predictions are 2336°C for melting, 4262°C for boiling, and 12.55 $g\ cm^{-3}$ for the density. The experimental values are 2172°C for melting, to which the prediction comes reasonably close, 4877°C for boiling, and 11.50 $g\ cm^{-3}$ for the density.

3.4 The predicted formulas are GeH_4, HF, H_2Te, BiH_3.

3.6 (a) Xe should have a higher IE_1 than Bi because of its closed-shell configuration.

(b) Selenium (Se) should have a higher IE_1 than Te; the two are in the same group and Se is higher up the periodic table.

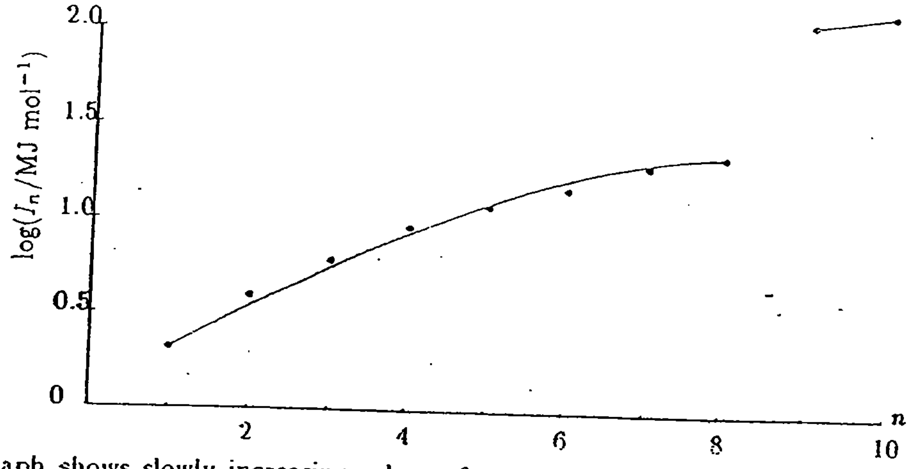
(c) Yttrium (Y) should have a higher IE_1 than Rb. The two are in the same row and Y is farther to the right.

(d) Neon (Ne) should have a higher IE_1 than K since its IE_1 exceeds that of Ar, which definitely has a higher IE_1 than K.

3.8 For Ne, data from Table 3.1 give

n	I_n/MJ mol^{-1}	log(I_n/MJ mol^{-1})	n	I_n/MJ mol^{-1}	log(I_n/MJ mol^{-1})
1	2.08	0.318	6	15.24	1.183
2	3.95	0.597	7	20.00	1.301
3	6.12	0.597	8	23.07	1.363
4	9.37	0.597	9	115.38	2.062
5	12.18	0.597	10	131.43	1.119

The graph of I_n vs. n follows



The graph shows slowly increasing values of $n = 1$ through $n = 8$ followed by an abrupt increase at $n = 9$. This suggests an outer shell of 8 electrons relatively easily removed, outside a very stable helium-like inner shell.

3.10 The reasoning uses the patterns in the periodic table as in problem 3.6:

(a) Rb (b) I (c) Te (d) Cl.

3.12 In < Sb < Se < S < Cl. The general trend is that electronegativity increases moving up a group (column) in the periodic table and moving from left to right across the groups from I toward VIII. Thus, electronegativity generally increases in a diagonal direction from lower left to upper right in the periodic table.

3.14 (a) $(\mathrm{Ra})^{2+}$ 86 electrons (0 valence, 86 core)

(b) $:\overset{..}{\underset{..}{\mathrm{Br}}}\cdot$ 35 electrons (7 valence, 28 core)

(c) $(:\overset{..}{\underset{..}{\mathrm{Bi}}}\cdot)^{2-}$ 85 electrons (7 valence, 78 core)

(d) $(\cdot\mathrm{Ga}\cdot)^{+}$ 30 electrons (2 valence, 28 core)

3.16 (a) $GaBr_3$, gallium bromide $\cdot\overset{\cdot}{\mathrm{Ga}}\cdot + 3\ :\overset{..}{\underset{..}{\mathrm{Br}}}\cdot \rightarrow (\mathrm{Ga}^{3+})(:\overset{..}{\underset{..}{\mathrm{Br}}}:^{-})_3$

(b) SrPo, strontium polonide $\cdot\mathrm{Sr}\cdot + \cdot\overset{..}{\underset{..}{\mathrm{Po}}}\cdot \rightarrow (\mathrm{Sr}^{2+})(:\overset{..}{\underset{..}{\mathrm{Po}}}:^{2-})$

(c) MgI_2, magnesium iodide $\cdot\mathrm{Mg}\cdot + 2\ :\overset{..}{\underset{..}{\mathrm{I}}}\cdot \rightarrow (\mathrm{Mg}^{2+})(:\overset{..}{\underset{..}{\mathrm{I}}}:^{-})_2$

(d) Li_2Se, lithium selenide $2\ \mathrm{Li}\cdot + \cdot\overset{..}{\underset{..}{\mathrm{Se}}}\cdot \rightarrow (\mathrm{Li}^{+})_2(:\overset{..}{\underset{..}{\mathrm{Se}}}:^{2-})$

3.18 (a) potassium nitrite (b) strontium permanganate (c) magnesium dichromate (d) sodium dihydrogen phosphate (e) barium chloride (f) sodium chlorate

3.20 (a) Cs_2SO_3 (b) $Sr(SCN)_2$ (c) LiH (d) Na_2O_2 (e) $(NH_4)_2Cr_2O_7$ (f) $RbHSO_4$

3.22 The formula is $NH_4H_2PO_4$, and the systematic name is ammonium dihydrogen phosphate.

3.24 The overall process $RbF(g) \rightarrow Rb(g) + F(g)$ can be seen as the sum of three steps:

$$\begin{array}{rrcll}
 & RbF(g) & \rightarrow & Rb^+(g) + F^-(g) & \Delta E_1 \\
 & Rb^+(g) + e^- & \rightarrow & Rb(g) & \Delta E = -IE_1(Rb) \\
 & F^-(g) & \rightarrow & F(g) + e^- & \Delta E = EA(F) \\
\hline
\text{Total} & RbF(g) & \rightarrow & Rb(g) + F(g) & \Delta E_{\text{total}}
\end{array}$$

The energy change for the first step is found by assuming the RbF to be ionic. The energy to separate an Rb^+ ion and an F^- ion, initially 2.274×10^{-10} m apart, is

$$\Delta E_1 = \frac{e^2}{4\pi\epsilon_o R} = \frac{(1.602 \times 10^{-19}\ \text{C})^2}{4\pi(8.854 \times 10^{-12}\ \text{C}^2\ \text{J}^{-1}\ \text{m}^{-1})(2.274 \times 10^{-10}\ \text{m})}$$
$$= 1.014 \times 10^{-18}\ \text{J} = 611\ \text{kJ mol}^{-1}$$

The dissociation energy of RbF to Rb and F is

$$\Delta E_{\text{total}} = \Delta E_1 - IE_1(\text{Rb}) + EA(\text{F}) = 611 - 403 + 328 = 536\ \text{kJ mol}^{-1}$$

This is close to the experimental value of 489 kJ mol^{-1}.

3.26 The order of bond length is ClF < BrCl < IBr. The smallest bond energy should be for the longest bond, the one in IBr.

3.28 (a) The formal charge on the central chlorine atom is +3; all four oxygen atoms have formal charges of −1.

(b) The formal charge of the central sulfur in the Lewis diagram for sulfur dioxide is +1; the left-hand oxygen has a formal charge of −1, and the right-hand oxygen has a formal charge of 0.

(c) The formal charge on the central bromine in this representation of the bonding in the bromite ion is +1. The two oxygens both have formal charges of −1.

(d) The formal charge on the central nitrogen in this Lewis diagram for nitrate ion is +1. The left-hand oxygen has a formal charge of 0, and the other two oxygen atoms have formal charges of −1.

3.30 In the Cl–Cl–O structure, the central Cl atom has formal charge +1 and the O atom has formal charge −1. In the Cl–O–Cl structure, each atom has formal charge zero. The second structure is favored because it shows less separation of formal charge.

3.32 (a) The "Z" represents a Group V element, such as N.

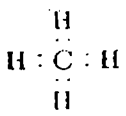
(b) The unknown main group element is a Group VII element, such as Cl.

(c) The unknown main group element is a Group VI element, such as S.

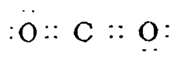
(d) The "Z" is a Group V element, such as N.

3.34 The Lewis dot structures are

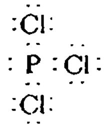
(a)



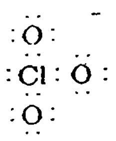
(b)



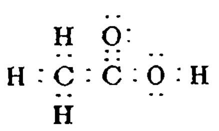
(c)



(d)



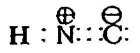
3.36 The best single Lewis structure is



The C–H bond lengths are estimated to be 1.10×10^{-10} m, the C–C bond length is 1.54×10^{-10} m, the C=O bond length is 1.20×10^{-10} m, the C–O bond length is 1.43×10^{-10} m, and the O–H bond length is 0.96×10^{-10} m.

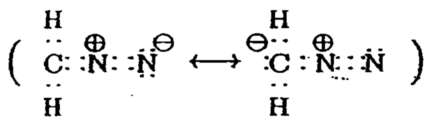
3.38 Each of the four phosphorus atoms has a lone pair of electrons. This accounts for 8 electrons. Each of the six dotted lines is replaced by a pair of electrons. This uses 12 electrons. Thus 20 electrons are used. These 20 electrons are all the valence electrons furnished by the four P atoms in P_4.

3.40 (a)

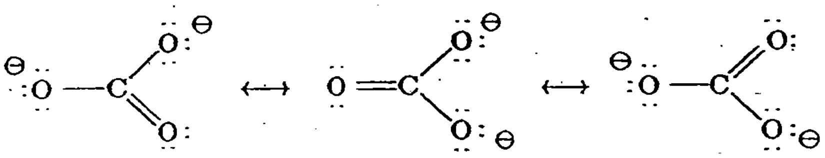


(b)

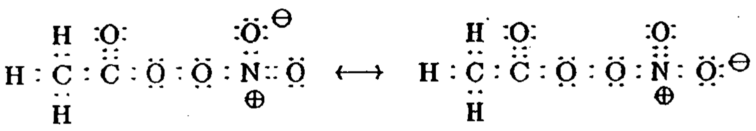
(c)



3.42 The carbon-oxygen bond lengths should fall between the values for a double bond (1.20×10^{-10} m) and for a single bond (1.43×10^{-10} m).

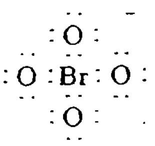


3.44

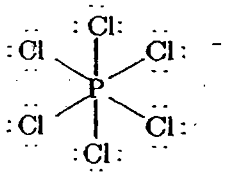


3.46 The valence octet is expanded in parts (b) and (c).

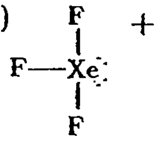
(a)



(b)



(c)



3.48 (a) $MgBr_2$ is more ionic than PBr_3 and should have a higher boiling point.

(b) SrO should boil higher than OsO_4 for the same reason.

(c) Al_2O_3 should boil higher than Cl_2O.

3.50

$$\delta = \frac{(0.2082\ \text{Å debye}^{-1})}{R}\mu = \frac{0.2082\ \text{Å D}^{-1}}{0.980\ \text{Å}}(1.66\ \text{D}) = 0.353 \text{ for OH } (35.3\%)$$

$$\delta = \frac{0.2082\ \text{Å D}^{-1}}{1.131\ \text{Å}}(1.46\ \text{D}) = 0.269 \text{ for CH } (26.9\%)$$

$$\delta = \frac{0.2082\ \text{Å D}^{-1}}{1.175\ \text{Å}}(1.45\ \text{D}) = 0.257 \text{ for CN } (25.7\%)$$

$$\delta = 0 \text{ for } C_2$$

3.52 The third and fourth columns of the following table present the comparison. Note that the absolute value of Δ must always be substituted in the equation.

Compound	Δ	$16\Delta + 3.5\Delta^2$	Expt. Ionic Character
ClF	0.82	15	11%
BrF	1.02	20	15%
BrCl	0.20	3.3	5.6%
ICl	0.50	8.9	5.8%
IBr	0.30	5.1	10%

3.54 (a) Phosphorus trifluoride has a central P with *SN* 4. The molecule is trigonal pyramidal, like NH_3 (text Figure 3.6(c)).

(b) Sulfuryl chloride has a central S with *SN* 4. The molecule is close to tetrahedral, but somewhat distorted because of the different steric requirements of the O's and Cl's.

(c) The PF_6^- anion has a central P with *SN* 6. The anion is octahedral.

(d) The ClO_2^- anion has a central Cl with *SN* 4. The anion is bent.

(e) Germanium hydride has a central Ge with *SN* 4. It is tetrahedral.

3.56 (a) In TeH_2, the central Te has *SN* 4. This molecule is bent.

(b) In AsF_3, the central As has *SN* 4. The molecule is a trigonal pyramid in which the F—As—F is distorted to somewhat less than the tetrahedral value of 109.5°.

(c) In PCl_4^+, the central P has *SN* 4. The molecular ion is an undistorted tetrahedron of Cl atoms about the central P.

(d) In XeF_5^+, the central Xe has *SN* 6. The molecular ion is a square pyramid with the four angles F_{eq}—Xe—F_{ax} distorted to less than 90°.

3.58 There are many possible answers for each part. Examples: (a) ClO_4^- (b) CO_2 (c) SbF_6^- (d) ClO_3^-

3.60 (a) Polar. (b) Polar. (c) Nonpolar. (d) Polar. (e) Nonpolar.

3.62 (a) Using VSEPR concepts, the $GaCl_4^-$ ion has a central Ga with steric number 4; it would be tetrahedral. The $SbCl_4^-$ ion has a central Sb with *SN* 5. It would have a seesaw geometry (text Figure 3.14(b)) since one of the five electron pairs is a lone pair.

(b) The $SbCl_2^+$ ion, in which the central Sb has *SN* 3, is a bent molecular ion, and the $GaCl_2^+$ ion, in which the central Ga has *SN* 2, is linear. It follows that the formulation $(SbCl_2^+)(GaCl_4^-)$ is more likely correct.

3.64 (a) The observation of a nonzero dipole moment for O_3 rules out a symmetrical linear geometry for the molecule. The molecule of ozone could be linear if the two O-to-O bonds were of different lengths, or if the molecule were bent.

(b) VSEPR assigns a steric number of 3 to the central O and predicts that the molecule of ozone is bent.

3.66 $\overset{-3}{N}\overset{+1}{H_4}\overset{+5}{N}\overset{-2}{O_3}$ $\quad\overset{+2}{Ca}\overset{+2}{Mg}\overset{+4}{Si}\overset{-2}{O_4}$ $\quad\overset{+2}{Fe}(\overset{+2}{C}\overset{-3}{N})_6^{4-}$ $\quad\overset{-3}{B_2}\overset{+1}{H_6}$

$\overset{+2}{Ba}\overset{-1}{H_2}$ $\quad\overset{+2}{Pb}\overset{-1}{Cl_2}$ $\quad\overset{+2}{Cu_2}\overset{-2}{O}(\overset{+6}{S}\overset{-2}{O_4})$ $\quad(\overset{+\frac{5}{2}}{S_4}\overset{-2}{O_6})^{2-}$

The choices for C and N in $Fe(CN)_6^{4-}$ were somewhat arbitrary; other choices are possible.

3.68 (a) La_2S_3 (b) Cs_2SO_4 (c) N_2O_3
(d) IF_5 (e) $Cr_2(SO_4)_3$ (f) $KMnO_4$

3.70 (a) magnesium silicate

(b) iron(II) hydroxide; iron (III) hydroxide

(c) diarsenic pentaoxide or arsenic(V) oxide

(d) ammonium hydrogen phosphate

(e) selenium hexafluoride

(f) mercury(I) sulfate

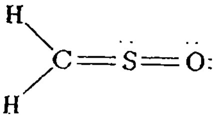
3.72 The difference in electronegativity between Rb and Cs is small, only 0.03, but the difference in electronegativity between Au and Cs is large, 1.75. This is slightly larger that ΔEN in NaI. The compound between Cs and Au can reasonably be formulated $Cs^+ \cdots Au^-$.

3.74 (a) The ΔE of the first reaction is the ionization energy IE_1 of Na(g) (multiplied by one mole) added to the negative of the *EA* (electron affinity) of I (also multiplied by 1 mol). Taking the values from Appendix F gives $\Delta E = 495.8 + (-295.2) = 200.6$ kJ. The ΔE of the second reaction is the *IE* of 1 mol of I added to the negative of the electron affinity of 1 mol of Na. It is $\Delta E = 1008.4 + (-52.867) = 955.5$ kJ.

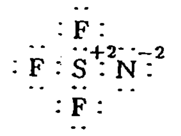
(b) Similar combination of the ionization energies and electron affinities of K and Cl gives ΔE of the first reaction as 69.8 kJ and ΔE of the second reaction as 1202.7 kJ. Even if Na^-I^+ or K^-Cl^+ were to form, the reactions transferring electrons to form Na^+I^- or K^+Cl^- would be strongly favored energetically and would occur quickly.

3.76 (a) In the Lewis structure on the left, the hydrogens and the carbon have formal charges of 0; the sulfur has a formal charge of +1, and the oxygen has a formal charge of −1. In the structure on the right, the hydrogens and the oxygen have zero formal charges; the carbon has a −1 formal charge and the sulfur has a +1 formal charge.

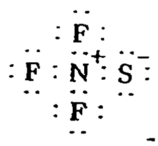
(b) The only way to draw a Lewis structure for the molecule of sulfine in which all atoms have formal charges of zero is to violate the octet rule for the sulfur atom (which would have two double bonds and see a total of ten valence electrons).



3.78 (a) Lewis diagrams for the suggested isomers of SF_3N follow. The octet rule is satisfied on all the atoms in these structures.

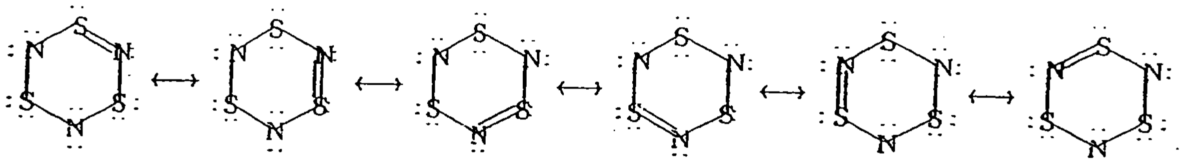


and



(b) Of the two structures shown, the one having the central N (on the right) is preferred. It has smaller formal charges. Additional resonance structures for both isomers are possible. Re-positioning four electrons in the structure on the left from lone pairs on the N to shared pairs between the N and S leads to an S≡N triple bond and formal charges of zero on all atoms. Doing this violates the octet rule for the central S, but such violations are known.

3.80 (a)



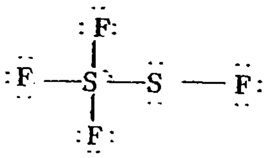
(b) In every resonance structure, the S that is involved in the double bond has a formal charge of +1 while the two N's that are *not* involved in the double bond have formal charges of −1. The other N and S's have formal charges of zero.

(c) Each S atom has a charge of $+\frac{1}{3}$, and each N atom of $-\frac{2}{3}$.

(d) Total charge $= 3(-0.375) + 3(+0.041) = -1.002 \approx -1$

3.82 (a) $^{\oplus}\ddot{\text{Cl}}=\overset{-2}{\text{Be}}=\ddot{\text{Cl}}^{\oplus}$ (b) $:\ddot{\text{Cl}}-\text{Be}-\ddot{\text{Cl}}:$

3.84 A Lewis structure for the monomer is $:\ddot{\text{F}}-\ddot{\text{S}}-\ddot{\text{F}}:$ and the dimer is



Valence expansion is necessary for S_2F_4.

3.86 For KCl(*g*)

$$\mu = 10.3\text{ D}; \quad R = 2.67\text{ Å}$$

If the $KCl(g)$ molecule were completely ionic, its dipole moment would be

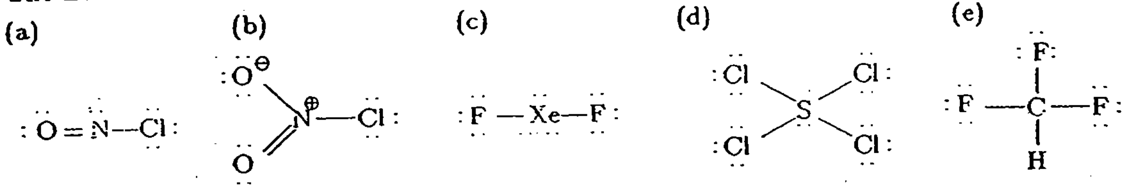
$$\mu = \frac{2.67 \times 10^{-10}\ \text{m} \times 1.602 \times 10^{-19}\ \text{C}}{3.336 \times 10^{-30}\ \text{C m D}^{-1}} = 12.82\ \text{D}$$

As it is, the degree of ionicity is not unity, but

$$\delta = \frac{10.3\ \text{D}}{12.82\ \text{D}} = 0.803\ (80.3\%)$$

3.88 The steric number of the central Xe in XeF_2 is 5; the molecule is linear. In XeF_4, the *SN* of the central Xe is 6; the molecule is square planar. In XeO_3, the *SN* of the central Xe is 4; the molecule is pyramidal (like ammonia). In XeO_4, the *SN* of the central Xe is 4; the molecule is tetrahedral. In H_4XeO_6, the 6 O's are bonded to a central Xe that has *SN* 6. The molecule is octahedral with H's on four of the six oxygen atoms. In $XeOF_4$, the central Xe has *SN* 6. The molecule consists of a square pyramid surrounding the Xe with the 4 F's at the corners of the base and the O at the apex (this allows the greatest distance between the lone pair and the O).

3.90 The Lewis dot structures are:



The NOCl molecule is bent and polar; the O_2NCl molecule is (nearly) trigonal about the N and polar; the XeF_2 molecule is linear and non-polar; the SCl_4 molecule has a seesaw geometry and is polar; the CHF_3 molecule is (nearly) tetrahedral and polar.

3.92 $2\,\overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} \rightarrow \overset{+1}{K_2}\overset{+6}{Mn}\overset{-2}{O_4} + \overset{+4}{Mn}\overset{-2}{O_2} + \overset{0}{O_2}$

Of the two Mn atoms, one gains one electron, and the other gains three, for a total of four. Two oxygen atoms each give up two electrons to provide these four electrons.

3.94 Hydrogen forms a +1 ion in many of its compounds, just like the metals of Group I. The +1 oxidation state in fact predominates in its chemistry. On the other hand, it is a gas not a metal at room conditions like the elements of Group VII). Also, in some situations (metal hydrides) it does form a −1 ion like the elements of Group VII.

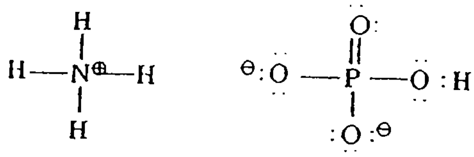
3.96 Element 114 is a group IV element that should have a maximum oxidation state of +4. However, the chemistry of heavier elements in this group (such as Pb) is dominated by the +2 oxidation state, so this should be true of element 114 as well.

3.98 Assume we have 100.00 g of compound and use the procedure of Chapter 1 to find the chemical amounts of each of the elements by dividing masses by molar masses:

$$\frac{48.46\ \text{g O}}{15.9994\ \text{g mol}^{-1}} = 3.029\ \text{mol O} \qquad \frac{23.45\ \text{g P}}{30.97376\ \text{g mol}^{-1}} = 0.7571\ \text{mol P}$$

$$\frac{21.21\ \text{g N}}{14.0067\ \text{g mol}^{-1}} = 1.514\ \text{mol N} \qquad \frac{6.87\ \text{g H}}{1.00794\ \text{g mol}^{-1}} = 6.816\ \text{mol H}$$

Divide each by the smallest one to find the formula $PO_4N_2H_9$, which is $(NH_4)_2HPO_4$, or ammonium hydrogen phosphate. The Lewis structures of the two ions are:



3.100 (a) Ammonium phosphate is $(NH_4)_3PO_4$; potassium nitrate is KNO_3; ammonium sulfate is $(NH_4)_2SO_4$.

(b) $(NH_4)_3PO_4$. First calculate the molecular masses by summing up the individual atomic masses of each element in the compound multiplied by the number of times it appears in the compound. Next, compute ratios of the individual masses of each element in the compound to the total molecular mass and convert to percentages:

Compound	Molecular Mass	Percent N	Percent P	Percent K
$(NH_4)_3PO_4$	149.09	28.18	20.78	0
KNO_3	101.10	13.85	0	38.67
$(NH_4)_2SO_4$	132.14	21.20	0	0

Chapter 4

The Gaseous State

4.2 The products of this reaction are easily predicted in the context; the balanced equation is $NH_4CO_2NH_2(s) \rightarrow 2\,NH_3(g) + CO_2(g)$. When predicting the products of a reaction, look for small stable molecules (like those of water, carbon dioxide or ammonia) that might be split off by larger molecules.

4.4 The acidification of aqueous solutions of KCN causes poisonous $HCN(g)$ to bubble out of the solution: $CN^-(aq) + H^+(aq) \rightarrow HCN(g)$.

4.6 (a)

$$\begin{aligned} P = \rho g h &= (13.60 \times 10^3 \text{ kg m}^{-3})(9.807 \text{ m s}^{-2})(0.0950 \text{ m}) \\ &= 1.267 \times 10^4 \text{ Pa} = 0.125 \text{ atm} \end{aligned}$$

(b)

$$\begin{aligned} \rho_1 g h_1 &= \rho_2 g h_2 \\ h_2 = \frac{\rho_1}{\rho_2} h_1 &= \left(\frac{13.60 \text{ g cm}^{-3}}{1.045 \text{ g cm}^{-3}}\right)(9.50 \text{ cm}) = 124 \text{ cm} = 1.24 \text{ m} \end{aligned}$$

4.8 A 76 cm column of mercury exerts the same pressure at its base that the atmosphere does on the earth at sea level. The density of the mercury in such a column is 13.6 g cm^{-3} (which is the same as 13.6×10^3 g L^{-1}) and is uniform over the length of the column. If a fluid with a uniform density of only 1.3 g L^{-1} replaces the mercury, it clearly must be substantially longer to exert the same pressure. It is in fact longer in proportion to the ratio of the densities. The thickness of the hypothetical atmosphere is thus

$$76 \text{ cm} \times \left(\frac{13.6 \times 10^3 \text{ g L}^{-1}}{1.3 \text{ g L}^{-1}}\right) = 8.0 \times 10^5 \text{ cm} = 8.0 \text{ km}$$

Unlike the ocean (problem 4-7), the atmosphere is nowhere near uniform in density. Its attenuation with altitude means that it must be much thicker than 8 km to exert a pressure of 1 atm.

4.10 The conversions can be carried out using the information in Table 4.2 in the text:

$$5 \times 10^{-10} \text{ torr} \times \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 7 \times 10^{-13} \text{ atm}$$

$$5 \times 10^{-10}\ \text{torr} \times \left(\frac{1\ \text{atm}}{760\ \text{torr}}\right) \times \left(\frac{1.01325 \times 10^{5}\ \text{Pa}}{1\ \text{atm}}\right) = 7 \times 10^{-8}\ \text{Pa}$$

4.12 Boyle's law applies to an expansion at constant temperature. The computation is

$$P_2 = \left(\frac{V_1}{V_2}\right) P_1 = \left(\frac{0.350\ \text{L}}{1.31\ \text{L}}\right)(1.23\ \text{atm}) = 0.329\ \text{atm}$$

4.14 Only in terms of the absolute temperature T is it correct to write

$$V_2 = \left(\frac{T_2}{T_1}\right) V_1$$

Converting the Celsius temperatures given in the problem to absolute temperatures and substituting gives

$$V_2 = \left(\frac{313.15\ \text{K}}{293.15\ \text{K}}\right)(4.00\ \text{L}) = 4.27\ \text{L}$$

4.16 The problem illustrates the operation of a gas thermometer. The temperature of a sample of an ideal gas is directly proportional to the absolute temperature as long as the pressure and the amount of gas in the sample do not change. Hence

$$T_2 = \left(\frac{V_2}{V_1}\right) T_1$$

If the temperature is converted from the Celsius scale to the Kelvin scale and the volumes are substituted:

$$T_2 = \left(\frac{5.26\ \text{L}}{5.40\ \text{L}}\right) \times 299.65\ \text{K} = 291.88\ \text{K}$$

Converting back to the Celsius scale gives 18.7°C.

4.18 This problem uses Charles's law, as in 4.16, but now a volume is to be determined:

$$V_2 = \left(\frac{T_2}{T_1}\right) V_1$$

T_2 is 503.15 K and T_1 is 293.15 K. Substituting gives

$$V_2 = \left(\frac{503.15\ \text{K}}{293.15\ \text{K}}\right) \times 3.41\ \text{L} = 5.85\ \text{L}$$

4.20 To prevent dangerous spurting from the container, the pressure inside must be brought below 0.96 atm. The pressure at 20°C (293.15 K) is 1.47 atm, and the pressure of an ideal gas at constant volume is directly proportional to the absolute temperature. Because $0.96/1.47 = 0.653$, the required absolute temperature is $0.653 \times 293.15 = 191.4$ K. Subtracting 273.15 K from this Kelvin temperature and multiplying the result by 1°C/1 K converts to −82°C.

4.22 The amount of gas n does not change when T and P change, so:

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

Solving for V_2 gives

$$V_2 = \left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)V_1$$

Substitution of $P_1 = 0.459$ atm, $P_2 = 0.980$ atm, $T_1 = 573.15$ K, $T_2 = 673.15$ K, and $V_1 = 63.6P$ L gives $V_2 = 35.0$ L.

4.24 (a) First we calculate the chemical amount of O_2 corresponding to 0.30 kg of O_2. It is 9.375 mol O_2. Assuming that O_2 is an ideal gas, we then calculate its pressure in the scuba tank:

$$P = \frac{nRT}{V} = \frac{9.375 \text{ mol } (0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})278.15 \text{ K}}{2.32 \text{ L}}$$
$$= 92 \text{ atm} = 1.4 \times 10^3 \text{ psi}$$

(b)

$$V_2 = \left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)V_1 = \left(\frac{92 \text{ atm}}{0.98 \text{ atm}}\right)\left(\frac{303 \text{ K}}{278 \text{ K}}\right)(2.32 \text{ L}) = 2.4 \times 10^2 \text{ L}$$

4.26 (a) The chemical equation is $2\,Al + 6\,HCl \rightarrow 3\,H_2 + 2\,AlCl_3$.

(b) Assume that the hydrogen behaves ideally and substitute the volume, pressure, and absolute temperature into the ideal gas equation:

$$n_{H_2} = \frac{PV}{RT} = \frac{(0.750 \text{ L})(10.0 \text{ atm})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(303.15 \text{ K})} = 0.3015 \text{ mol}$$

According to the balanced equation, 2/3 this amount of aluminum must react. The chemical amount of Al is therefore 0.2010 mol, and the mass of Al is 0.2010 mol multiplied by 26.98 g mol^{-1}. This answer is 5.42 g Al.

4.28 (a) $Fe(s) + H_2SO_4(aq) \rightarrow H_2(g) + FeSO_4(aq)$.

(b) The 300×10^3 g mass of sulfuric acid is converted to chemical amount by dividing by its molar mass (98.08 g mol^{-1}). The equation states that 1 mol of H_2 forms for every 1 mol of H_2SO_4, so the reaction gives 3.059×10^3 mol of H_2. Substituting this value as n in the ideal-gas equation with $T = 300$ K and $P = 1.0$ atm gives $V = 7.5 \times 10^4$ L.

(c) The formula $V = 4/3\pi r^3$ relates the volume of a sphere to its radius. A liter is equal to a cubic decimeter, so inserting the volume of gas in liters into this formula and solving for r gives the radius of the spherical balloon in decimeters. It is 26 dm, which is 2.6 m (8.6 feet).

4.30 Using the ideal gas law for chlorine gives its number of moles as

$$n = \frac{PV}{RT} = \frac{(0.953 \text{ atm})(5.32 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(306.15 \text{ K})} = 0.2018 \text{ mol}$$

This is also the chemical amount of MnO_2 reacting, because one mole of MnO_2 generates one mole of Cl_2. The mass is then found by multiplying by the molar mass of MnO_2, 86.937 g mol^{-1}, to give 17.5 g MnO_2.

4.32 Divide the mass of KO_3, 4.69 g, by its molar mass, 87.10 g mol^{-1}, to find the chemical amount of KO_3, 0.05385 mol. The chemical amount of ozone is then

$$\left(\frac{5 \text{ mol } O_3}{2 \text{ mol } KO_3}\right) \times (0.05385 \text{ mol } KO_3) = 0.1346 \text{ mol } O_3$$

From the ideal gas law,

$$V = \frac{nRT}{P} = \frac{(0.1346\ \text{mol})(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(258.15\ \text{K})}{0.134\ \text{atm}} = 21.3\ \text{L}$$

4.34 The total chemical amount of gas in the reaction mixture is 13 + 31 + 93 = 137 mol. The ammonia contributes 13 mol so its mole fraction is 13/137 = 0.095. The partial pressure of the ammonia is simply its mole fraction multiplied by the total pressure, as long as the mixture behaves according to Dalton's law. Then $P_{NH_3} = 20$ atm.

4.36 For ideal gas mixtures, mole fractions are the same as fractions by volume, so the mole fraction of N_2 is 0.035. Its partial pressure is the mole fraction multiplied by the total pressure, giving 3.2 atm.

4.38 (a) Before the reaction, the mole fraction of the Br_2 is 4.5/(4.5 + 33.1) = 0.12.

(b) According to the balanced equation, the formation of 2.2 mol of BrF_5 consumes 1.1 mol of Br_2 and 5.5 mol of F_2. At the indicated point in the reaction, there are 3.4 mol of Br_2 and 27.6 mol of F_2 left. This plus the 2.2 mol of BrF_5 means that there is 33.2 mol of substances of all kinds present. The mole fraction of Br_2 is 3.4/33.2 = 0.10. Despite the fact that about a quarter of the Br_2 has been consumed, the mole fraction of Br_2 has dropped by only a sixth.

4.40 (a)

$$n_{O_2} = \frac{PV}{RT} = \frac{(0.200\ \text{atm})(1.500\ \text{L})}{(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(313.15\ \text{K})} = 1.167 \times 10^{-2}\ \text{mol O}_2$$

$$N_{O_2} = (1.167 \times 10^{-2}\ \text{mol})(6.022 \times 10^{23}\ \text{mol}^{-1}) = 7.03 \times 10^{21}\ \text{molecules}$$

(b) Oxygen is the limiting reactant. $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

$$n_{H_2O} = \left(\frac{2\ \text{mol H}_2\text{O}}{1\ \text{mol O}_2}\right)(1.167 \times 10^{-2}\ \text{mol O}_2) = 2.335 \times 10^{-2}\ \text{mol}$$

$$m_{H_2O} = (2.335 \times 10^{-2}\ \text{mol})(18.02\ \text{g mol}^{-1}) = 0.421\ \text{g}$$

4.42 The relationship between the root-mean-square speed of the molecules of a gas and the temperature of the gas is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}} = \sqrt{\frac{3(8.3145\ \text{J K}^{-1}\text{mol}^{-1})(0.00024\ \text{K})}{0.023\ \text{kg mol}^{-1}}} = 0.51\ \text{m s}^{-1}$$

Common errors here are to use $\mathcal{M}$ in g mol^{-1} instead of kg mol^{-1} or to use R in the wrong units.

4.44 To calculate the rms speeds of helium, argon, and xenon atoms at 2000 K we substitute the molar masses in kg mol^{-1} of the three gases successively into the expression

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

taking $T = 2000$ K and $R = 8.3145$ J K^{-1}mol^{-1}. The answers are 3.53 km s^{-1} for helium, 1.12 km s^{-1} for argon and 0.616 km s^{-1} for xenon. These values are respectively 31.5%, 10.0% and 5.50% of the earth's escape velocity. Helium is much more likely to escape than the heavier gases.

4.46 Molecules of Cl_2 have a greater mass than those of ClO_2. At a given temperature, the speed distribution of heavier molecules is shifted to lower values. Thus the percentage of chlorine molecules with speeds in excess of 400 m s^{-1} will be less than 35%.

4.48

$$\text{Moles escaping} = \frac{(0.001\text{ atm})(0.200\text{ L})}{(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})(298\text{ K})} = 8.18 \times 10^{-6}\text{ mol}$$

$$\begin{aligned}
Z_w &= \text{molecules escaping per second}\\
&= \frac{(8.18 \times 10^{-6}\text{ mol})(6.022 \times 10^{23}\text{ mol}^{-1})}{3600\text{ s}} = 1.37 \times 10^{15}\text{ s}^{-1}\\
&= \frac{1}{4}\frac{N}{V}\bar{u}A = \frac{1}{4}\frac{N_0 P}{RT}\bar{u}A\\
\bar{u} &= \sqrt{\frac{8RT}{\pi\mathcal{M}}} = \sqrt{\frac{8(8.3145\text{ J mol}^{-1}\text{ K}^{-1})(298\text{ K})}{\pi(2.016 \times 10^{-3}\text{ kg mol}^{-1})}} = 1770\text{ m s}^{-1}\\
A &= \frac{4RT\,Z_w}{N_0 P\bar{u}}\\
&= \frac{4(8.3145\text{ J mol}^{-1}\text{ K}^{-1})(298\text{ K})(1.37 \times 10^{15}\text{ s}^{-1})}{(6.022 \times 10^{23}\text{ mol}^{-1})(0.990\text{ atm})(101325\text{ Pa atm}^{-1})(1770\text{ m s}^{-1})}\\
&= 1.27 \times 10^{-13}\text{ m}
\end{aligned}$$

$$\text{Radius} = \sqrt{\frac{A}{\pi}} = 2 \times 10^{-7}\text{ m}$$

The proper choice of units for R is crucial in this problem.

4.50 The problem is a straightforward application of Graham's law of effusion. The relative rates of effusion are given by

$$\frac{\text{rate}_{F_2}}{\text{rate}_{BrF_5}} = \sqrt{\frac{\mathcal{M}_{BrF_5}}{\mathcal{M}_{F_2}}}$$

Substituting the molar masses gives 2.145 as the ratio of the rates of effusion. As effusion continues the remaining mixture becomes enriched in the heavier gas, and this ratio drops.

4.52

$$\frac{\text{rate (He)}}{\text{rate (H}_2\text{)}} = 3 = \frac{N(\text{He})}{N(\text{H}_2)}\sqrt{\frac{m(\text{H}_2)}{m(\text{He})}}$$

$$\frac{N(\text{He})}{N(\text{H}_2)} = 3\sqrt{\frac{m(\text{He})}{m(\text{H}_2)}} = 3\sqrt{1.986} = 4.227$$

$$X(\text{H}_2) = \frac{N(\text{H}_2)}{N(\text{H}_2) + N(\text{He})} = \frac{1}{1 + 4.23} = 0.191$$

The enrichment factor per stage is $\sqrt{1.986} = 1.409$. After n stages, the ratio is

$$\left(\frac{N(\text{H}_2)}{N(\text{He})}\right)_n = \left(\frac{N(\text{H}_2)}{N(\text{He})}\right)_0 (1.409)^n = \frac{1}{4.227}(1.409)^n$$

For 99.9% purity,

$$\frac{N(\mathrm{H_2})}{N(\mathrm{He})} = \frac{99.9}{0.1} = 999$$

$$999 = \frac{1}{4.227}(1.409)^n$$

$$4223 = (1.403)^n$$

$$\log_{10} 4223 = n \log_{10} 1.403$$

$$n = 24.7 \quad \text{Thus 25 stages are required.}$$

4.54

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V} = \frac{1}{\sqrt{2}\,\pi d^2 N_0 P/RT}$$

$$P = \frac{RT}{\sqrt{2}\pi d^2 \lambda N_0} = \frac{(8.3145\ \mathrm{J\ K^{-1}mol^{-1}})(300\ \mathrm{K})}{\sqrt{2}\pi(3.16 \times 10^{-10}\ \mathrm{m})^3(6.022 \times 10^{23}\ \mathrm{mol^{-1}})}$$

$$= 2.95 \times 10^7\ \mathrm{Pa} = 292\ \mathrm{atm}$$

At this temperature for Kr, $\bar{u} = \sqrt{8RT/\pi\mathcal{M}} = 275.3\ \mathrm{m\ s^{-1}}$

$$D = \frac{3\pi}{16}\lambda\bar{u} = 5.1 \times 10^{-8}\ \mathrm{m^2\ s^{-1}}$$

4.56 We solve the van der Waals equation for the pressure and substitute:

$$P = \frac{nRT}{V - nb} - a\left(\frac{n^2}{V^2}\right)$$

$$= \frac{(140 \times 10^6/18.0153)\ \mathrm{mol}(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})\,(813.15\ \mathrm{K})}{(2500 \times 10^3\ \mathrm{L}) - (140 \times 10^6/18.0153)\ \mathrm{mol}(0.03049\ \mathrm{L\ mol^{-1}})}$$

$$- (5.464\ \mathrm{atm\ L^2 mol^{-2}})\left(\frac{(140 \times 10^6/18.0153)^2(\mathrm{mol})^2}{(2500 \times 10^3\ \mathrm{L})^2}\right)$$

$$= 176\ \mathrm{atm} = 2590\ \mathrm{psi}$$

4.58 The chemical amount of methane is 60.0 g/16.04 g mol^{-1} = 3.74 mol.

(a) Using the ideal gas equation

$$T = \frac{PV}{nR} = \frac{(130\ \mathrm{atm})(1.00\ \mathrm{L})}{(3.74\ \mathrm{mol})(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})} = 424\ \mathrm{K}$$

(b) Using the van der Waals equation

$$T = \frac{(P + an^2/V^2)(V - nb)}{nR} = \frac{(130 + 2.253(3.74)^2)\ \mathrm{atm}(1.00 - (3.74)(0.04278))\ \mathrm{L}}{(3.74\ \mathrm{mol})(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})} = 442\ \mathrm{K}$$

Because 442 K > 424 K, the a term (attractive forces) dominates under these conditions.

4.60

$$\begin{aligned} P = \rho g h &= (4.9 \times 10^3 \text{ kg m}^{-3})(9.80665 \text{ m s}^{-2})(9.0 \text{ ft})(0.3048 \text{ m ft}^{-1}) \\ &= 1.32 \times 10^5 \text{ kg m}^{-1}\text{ s}^{-2} = 1.32 \times 10^5 \text{ Pa} = 1.3 \text{ atm} \\ &= (1.3 \text{ atm})(14.696 \text{ lb in}^{-2} \text{ atm}^{-1}) = 19 \text{ psi} \end{aligned}$$

4.62 Setting $V = 0$ gives

$$\begin{aligned} -209.4 \text{ L} &= 0.456 \text{ L }^\circ\text{F}^{-1}\, t_f \\ t_f &= -459^\circ\text{F} \end{aligned}$$

4.64 Density $\propto \frac{n}{V} = \frac{P}{RT}$

At constant P, T changes from 323 K to 423 K. The density will be multiplied by the ratio 323/423.

$$\text{Density} = \left(\frac{323 \text{ K}}{423 \text{ K}}\right)(2.94 \text{ g L}^{-1}) = 2.24 \text{ g L}^{-1}$$

Consider one liter of gas at 50°, weighing 2.94 g. Then

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L atm}^{-1} \text{ mol}^{-1} \text{ K}^{-1})(323 \text{ K})} = 3.77 \times 10^{-2} \text{ mol}$$

$$\mathcal{M} = \frac{2.94 \text{ g}}{3.77 \times 10^{-2} \text{ mol}} = 77.9 \text{ g mol}^{-1}$$

4.66 (a) Assume that the dry air is an ideal gas. Its density is determined by combining the ideal gas equation with the relation $n = m/\mathcal{M}$ (where m is the mass of the gas, and $\mathcal{M}$ is the molar mass of the gas) and the definition of density ($\rho = m/V$) and rearranging to give

$$\rho = \frac{\mathcal{M}P}{RT}$$

A temperature of 95°F is 35.0°C or 308.15 K. Substituting this temperature, $P = 1.00$ atm, $\mathcal{M} = 29.0 \text{ g mol}^{-1}$, and $R = 0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}$ gives $\rho = 1.15 \text{ g L}^{-1}$.

(b) A temperature of 50°F is 10.0°C or 283.15 K. The method of part (a) gives the density of the cool dry air as $\rho = 1.25 \text{ g L}^{-1}$.

(c) Saturating dry air with water vapor means adding a component to the mixture that has a molar mass less that the $\mathcal{M}$'s of N_2 and O_2, the main components of dry air. The effective molar mass of moist air is therefore less than 29.0 g mol^{-1}. The density of a gas is directly proportional to its molar mass $\mathcal{M}$ (see part a). It follows that moist air is less dense than dry air at any given T and P. If a batted ball truly carries better in low-density air, then high humidity favors the home run.

4.68 A cubic foot is 28.317 L according to tables of conversion factors. This factor can also be computed: there are 12^3 cubic inches in a cubic foot and 2.54^3 cm^3 in a cubic inch, so a cubic foot is $12^3 \times 2.54^3 = 28\,316.8 \text{ cm}^3$ or 28.317 L. The 1.0 lb of Hydrone generates 2.6×28.317 L of hydrogen. Solving the ideal gas law for the chemical amount gives 3.285 mol of H_2. The balanced equation states that it takes 2 mol of Na to generate 1 mol of H_2. Hence, the Hydrone contains 6.57 mol of sodium. Because the molar mass of sodium is 23 g mol^{-1}, the 1.0 lb (453.59 g) of Hydrone contained 151 g of sodium. This is 33% of the mass of the Hydrone.

4.70 For every six molecules originally present, three (half) are consumed. These three react to give two new ones for a total of five molecules. If n is multiplied by $\frac{5}{6}$ with V and T constant, then P must be multiplied by $\frac{5}{6}$. This gives

$$P = \frac{5}{6}(0.740 \text{ atm}) = 0.617 \text{ atm}$$

4.72 $CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$

For every mole of $CS_2(g)$ that reacts, the total number of moles changes by 1. Because the temperature and volume are the same before and after, the initial partial pressure of CS_2 must be equal in magnitude to the change in total pressure, namely 3.00 − 2.40 = 0.60 atm.

$$n_{CS_2} = \frac{PV}{RT} = \frac{(0.60 \text{ atm})(10.0 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(373.15 \text{ K})} = 0.196 \text{ mol}$$

$$n_{CS_2} = (0.196 \text{ mol})(76.14 \text{ g mol}^{-1}) = 14.9 \text{ g}$$

4.74 (a) The volume of the trap is expressed in liters ($1 \text{ L} = 10^{-3} \text{ m}^3$) and the amount of its contents is expressed in moles ($n = 500/6.022 \times 10^{23} \text{ mol}^{-1} = 8.3029 \times 10^{-22}$). Then, the problem becomes a substitution into $PV = nRT$. Completing the arithmetic gives $P = 1.6 \times 10^{-14}$ atm. The pressure is very low. Otherwise the frail walls made of light would not contain the gas.

(b) The mean free path of the sodium atoms in the optical trap is

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_o P} = 3.9 \text{ m}$$

Solving for the diameter d gives 3.4×10^{-10} m. At room conditions in gaseous sodium the mean free path is about 8×10^{-8} m, smaller by a factor of 50,000,000.

4.76 (a)

$$KE \text{ per mole} = \frac{3}{2}RT$$

$$\text{average } KE \text{ per molecule} = \frac{3}{2}\frac{RT}{N_0}$$

$$= \frac{3}{2}\frac{(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(473 \text{ K})}{6.022 \times 10^{23} \text{ mol}^{-1}} = 9.80 \times 10^{-21} \text{ J at 200°C.}$$

At 400°C, this gives 1.39×10^{-20} J. Both results are independent of mass, and thus of oxygen isotopic composition.

(b) The average speed is

$$\bar{u} = \sqrt{\frac{8RT}{\pi \mathcal{M}}}$$

At 200°C, the combination of constants is

$$\frac{8RT}{\pi} = \frac{8(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(473 \text{ K})}{\pi} = 1.001 \times 10^4 \text{ J mol}^{-1}$$

The molar mass of the lightest species, $^{16}O^{16}O$, is (approximately) 32.0 g mol^{-1} and that of the heaviest, $^{18}O^{18}O$, is 36.0 g mol^{-1}. This gives average speeds of

$$\bar{u} = \sqrt{\frac{1.001 \times 10^4 \text{ J mol}^{-1}}{32.0 \times 10^{-3} \text{ kg mol}^{-1}}} = 559 \text{ m s}^{-1} \text{ for the lightest,}$$

and 527 m s^{-1} for the heaviest. At 400°C, the corresponding average speeds are 667 and 629 m s^{-1}.

4.78 (a) From the right angle geometry in the figure,

$$\begin{aligned} r\cos\theta &= \Delta l/2 \\ \Delta l &= 2r\cos\theta \end{aligned}$$

(b) Magnitude of momentum = mu

Component perpendicular to wall = $mu\cos\theta$

$$\Delta p_{\text{wall}} = mu\cos\theta - (-mu\cos\theta) = 2mu\cos\theta$$

(c) Time between collisions = $\frac{\Delta l}{u} = \Delta t$

Force on wall = $\frac{\Delta p_{\text{wall}}}{\Delta t} = \frac{2mu\cos\theta}{2r\cos\theta/u} = \frac{mu^2}{r}$

(d) From N molecules,

$$\text{force} = \frac{N m\overline{u^2}}{r}$$

The surface area of the sphere is $4\pi r^2$, so

$$P = \frac{\text{force}}{\text{area}} = \frac{N m\overline{u^2}}{4\pi r^2(r)}$$

The volume of the sphere is $V = \frac{4}{3}\pi r^3$. Multiplying by P gives

$$PV = \frac{1}{3}N m\overline{u^2}$$

4.80 The collision rate with the wall (in molecules per second) is

$$Z_W = \frac{1}{4}\frac{N}{V}\sqrt{\frac{8RT}{\pi\mathcal{M}}}A$$

Replacing N with n gives the rate in moles per second, then, from the ideal gas law

$$\frac{1}{4}\frac{n}{V}\sqrt{\frac{8RT}{\pi\mathcal{M}}}A = \frac{1}{4}P\sqrt{\frac{8}{\pi\mathcal{M}RT}}A$$

$$P = 2000 \text{ psi}\left(\frac{1 \text{ atm}}{14.696 \text{ psi}}\right)\left(\frac{101325 \text{ Pa}}{1 \text{ atm}}\right) = 1.38\times10^{7} \text{ Pa}$$

$$\mathcal{M} = 16.04\times10^{-3} \text{ kg mol}^{-1}$$

$$A = 1.0 \text{ mm}^2 = 1.0\times10^{-6} \text{ m}^2$$

$$\text{Rate} = \frac{1}{4}(1.38\times10^{7} \text{ Pa})\sqrt{\frac{8}{\pi(16.04\times10^{-3} \text{ kg mol}^{-1})(8.3145)(293 \text{ K})}}(1\times10^{-6} \text{ m}^2)$$

$$= 0.88 \text{ mol s}^{-1}$$

$$(0.88 \text{ mol s}^{-1})(60 \times 60 \times 24 \text{ s day}^{-1}) = 7.6 \times 10^4 \text{ mol day}^{-1}$$

$$(7.6 \times 10^4 \text{ mol day}^{-1})(16.04 \text{ g mol}^{-1}) = 1.2 \times 10^6 \text{ g day}^{-1}$$

$$\begin{aligned}\text{Volume of tank} &= \pi(20)^2(50) \text{ ft}^3 \times (0.3048 \text{ m ft}^{-1})^3 \\ &= 1.78 \times 10^3 \text{ m}^3 = 1.78 \times 10^6 \text{ L}\end{aligned}$$

$$n = \frac{PV}{RT} = \frac{(2000 \text{ psi}/14.696 \text{ psi atm}^{-1})(1.78 \times 10^6 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(293 \text{ K})} = 1.01 \times 10^7 \text{ mol}$$

$$\text{Fraction lost per day} = \frac{7.6 \times 10^4 \text{ mol}}{1.01 \times 10^7 \text{ mol}} = 0.0075$$

4.82 (a) $\frac{N}{V} = \frac{N_0 n}{V} = N_0 \frac{P}{RT}$

$$D = \frac{3}{8}\sqrt{\frac{RT}{\pi \mathcal{M}}}\frac{1}{d^2 N_0 \frac{P}{RT}} = \frac{3}{8}\frac{(RT)^{\frac{3}{2}}}{(\pi\mathcal{M})^{\frac{1}{2}} d^2 N_0 P}$$

Expressing everything in SI units gives

$$\begin{aligned}D &= \frac{3}{8}\frac{[(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(293 \text{ K})]^{\frac{3}{2}}}{[(\pi)(17 \times 10^{-3} \text{ kg mol}^{-1})]^{\frac{1}{2}}(3 \times 10^{-10} \text{ m})^2(6.02 \times 10^{23} \text{ mol}^{-1})(101325 \text{ Pa})} \\ &= 3.55 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}\end{aligned}$$

(b)

$$t = \frac{\overline{\Delta r^2}}{6D} = \frac{(100 \text{ m})^2}{6(3.55 \times 10^{-5} \text{ m}^2 \text{ s}^{-1})} = 4.7 \times 10^7 \text{ s} = 1.5 \text{ yr}$$

4.84 (a) It is easiest to convert the number density to density in moles per liter:

$$\frac{n}{V} = \frac{10 \text{ atoms}}{1 \text{ cm}^3} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = 1.66 \times 10^{-20} \text{ mol L}^{-1}$$

Substitution of this value into $P = (n/V)RT$ gives $P = 1.4 \times 10^{-19}$ atm.

(b) The root-mean-square speed is calculated by substituting $T = 100$ K and $\mathcal{M} = 1.008 \times 10^{-3}$ kg mol^{-1} into

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

being sure to use R in the proper units (J K^{-1}mol^{-1}). The answer is 1.57×10^3 m s^{-1}. Multiplying this speed by the time between collisions gives the distance between collisions, on the average. It is 1.57×10^{12} m, about 10.5 times the distance between the earth and the sun.

4.86 From Eq. 4-15, the rate at which a molecule collides with other molecules is

$$Z_1 = 4\frac{N}{V}d^2\sqrt{\frac{\pi RT}{\mathcal{M}}} = 4N_0\frac{P}{RT}d^2\sqrt{\frac{\pi RT}{\mathcal{M}}}$$

(a) Inserting $d = \sigma = 3.82 \times 10^{-10}$ m for methane, at 25°C and 1 atm pressure (101,325 Pa), gives a rate of 1.0×10^{10} s^{-1}.

(b) At $P = 1.0 \times 10^{-7}$ atm, the rate is 1.0×10^3 s^{-1}, smaller by a factor of 10^7.

4.88

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

$$F(R) = -\frac{dV(R)}{dR} = \frac{4\epsilon}{\sigma}\left[12(\sigma/R)^{13} - 6(\sigma/R)^{7}\right]$$

$$\sigma = 3.40\ \text{Å} = 3.40 \times 10^{-10}\ \text{m}$$

$$\epsilon = 1.654 \times 10^{-21}\ \text{J}$$

$$F(R) = \frac{24\epsilon}{\sigma}\left[2(\sigma/R)^{13} - (\sigma/R)^{7}\right] = (1.168 \times 10^{-10}\ \text{J m}^{-1})\left[2(\sigma/R)^{13} - (\sigma/R)^{7}\right]$$

At $3.0\ \text{Å} = 3.0 \times 10^{-10}\ \text{m},\ F(R) = 9.08 \times 10^{-10}\ \text{J m}^{-1}$
$3.4\ \text{Å} = 3.4 \times 10^{-10}\ \text{m},\ F(R) = 1.17 \times 10^{-10}\ \text{J m}^{-1}$
$3.8\ \text{Å} = 3.8 \times 10^{-10}\ \text{m},\ F(R) = 1.40 \times 10^{-12}\ \text{J m}^{-1}$
$4.2\ \text{Å} = 4.2 \times 10^{-10}\ \text{m},\ F(R) = -1.16 \times 10^{-11}\ \text{J m}^{-1}$

The force is repulsive at the first three distances, attractive at the fourth.

4.90

$$\frac{\text{Volume of chlorine}}{\text{Volume of compound}} = \frac{0.688\ \text{L}}{0.153\ \text{L}} = \frac{\text{Moles of Cl}_2}{\text{Moles of compound}} = 4.5$$

Each mole of compound thus contains 2 × 4.5 = 9 mol of Cl atoms. The chemical amount of compound comes from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1.00\ \text{atm})(0.153\ \text{L})}{(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(273.15\ \text{K})} = 6.83 \times 10^{-3}\ \text{mol}$$

The molar mass is the mass (2.842 g) divided by the chemical amount (6.83×10^{-3} mol), giving 416 g mol^{-1}. Subtracting 9 × 35.453 g mol^{-1} from the Cl leaves 97.3 g mol^{-1}. Dividing by the molar mass of B, 10.811 g mol^{-1}, gives 9.0, so the formula is B_9Cl_9. Note the similarities and differences between this problem and problem 2.44.

4.92 (a) The reaction is

$$Rb_2SO_3 + 2\ HBr \rightarrow 2\ RbBr + H_2O + SO_2$$

The initial chemical amount of Rb_2SO_3 is

$$\frac{6.24\ \text{g}}{251.0\ \text{g mol}^{-1}} = 0.02486\ \text{mol Rb}_2\text{SO}_3$$

The initial chemical amount of HBr is

$$n = \frac{PV}{RT} = \frac{(0.953\ \text{atm})(1.38\ \text{L})}{(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(348.15\ \text{K})} = 0.04603\ \text{mol HBr}$$

Because 2 mol of HBr reacts with 1 mol of Rb_2SO_3, the HBr will be used up first. It is the limiting reactant.

(b) Each mole of HBr that reacts should theoretically give one mole of RbBr. The theoretical yield is

$$(0.04603\ \text{mol RbBr})(165.37\ \text{g mol}^{-1}) = 7.61\ \text{g}$$

(c) The percentage yield is (7.32 g/7.61 g) × 100% = 96.2%.

Chapter 5

Solids, Liquids, and Phase Transitions

5.2 Because the substance is viscous and nearly incompressible, it is not a gas. Elasticity is closely related to rigidity and hardness, properties that are characteristic of solids rather than liquids. Hence, the substance is a liquid.

5.4 (a) The density of this substance is $57.9/18.3 = 3.16\ \mathrm{g\ L^{-1}} = 0.00316\ \mathrm{g\ cm^{-3}}$. Although the conditions of temperature and pressure are not given, it is hard to imagine a solid or liquid having such a low density regardless of conditions. Thus, a key to the problem is a knowledge of typical densities such as those of ice and water (approximately 0.9 and 1.0 $\mathrm{g\ cm^{-3}}$). Demonstrations are very useful in teaching this.

(b) The molar volume is the volume occupied by one mole of a substance. It equals the molar mass divided by the density or, equivalently, the molar mass multiplied by the reciprocal of the density:

$$\left(\frac{123\ \mathrm{g}}{1\ \mathrm{mol}}\right) \times \left(\frac{18.3 \times 10^3\ \mathrm{cm^3}}{57.9\ \mathrm{g}}\right) = 3.89 \times 10^4\ \frac{\mathrm{cm^3}}{\mathrm{mol}}$$

This large molar volume is quite consistent with the value quoted in the text for gases under typical conditions.

5.6 The same cooling of an ideal gas from 343.15 K to 283.15 K would decrease its volume to 0.825 of its original volume, where 0.825 is obtained as the ratio of 343.15 K to 283.15 K. This substance in fact decreases its volume to 0.816 of its original value. It is a nearly ideal gas.

5.8 In a gas there are only weak or nearly nonexistent intermolecular attractions so the molecules are not held strongly to each other. In solid and liquid metals, the intermolecular forces are large, so that the metal changes its volume little even with considerable increase in the temperature.

5.10 The surface tension of liquid NaCl should be higher than that of CCl_4 because the intermolecular forces in NaCl (ion-ion forces) are intrinsically stronger than the forces in CCl_4 (dispersion forces).

5.12 The kinetic theory predicts an increase in molecular speed in all three states of matter with increasing temperature. Since diffusion depends on the random motions of the molecule of substances, which become more rapid at higher temperature, the theory predicts that the diffusion constants should increase with temperature in all states of matter.

5.14 Dipole-dipole forces arise among particles with permanent dipoles, that is, among particles having pre-existent nonuniform charge distributions. Dispersion forces are sometimes called instantaneous dipole-induced dipole forces. They operate at shorter range than dipole-dipole forces and are weaker. Dipole-dipole forces are found in polar substances (such as $HCl(g)$); dispersion forces are found in all substances.

5.16 (a) dispersion forces (b) dipole-dipole forces (predominant) and dispersion forces (c) dispersion forces (d) ion-ion forces (predominant) and dispersion forces

5.18 An atom of argon should be most strongly attracted by an atom of krypton. The krypton atom has more electrons and is more polarizable than one of argon and the strength of dispersion forces depends on the polarizability of the interacting species.

5.20 False. A small atom such as hydrogen can approach another atom quite closely, whereas a weak chemical bond between a pair of large atoms can leave the atoms quite far apart.

5.22 The pentafluoride with the largest molar mass (IF_5) is the solid, the one with the second largest molar mass (BrF_5) is the liquid, and the one with the least molar mass (ClF_5) is the gas; the strength of attractive forces increases with increasing molar mass.

5.24 $He < Ar < SO_2 < HF < CaF_2$

Ar is heavier than He, while SO_2 is non-spherical and interacts through electrostatic forces. Hydrogen bonding is present for HF, while CaF_2 is bound by ionic forces.

5.26 The structure has chains of H—O—F molecules, which are bent, linked by O···H hydrogen bonds. The fluorine atoms stick out to the side of the chain.

5.28 Hydrogen peroxide will have extensive hydrogen bonding and display anomalies similar to those displayed by water. It should have a higher boiling point than F_2 and H_2S.

5.30 In $HF(l)$, one hydrogen bond is possible for every molecule of HF; in $H_2O(l)$, two hydrogen bonds are possible for every molecule of H_2O. The answers are therefore N_0 and $2N_0$.

5.32 Assume that helium vapor in equilibrium with liquid helium can be described by the ideal-gas equation. Rearranging the equation so that the molar volume is explicitly on the left and substituting the values from the problem gives

$$\frac{V}{n} = \frac{RT}{P} = \frac{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})2.20 \text{ K}}{0.05256 \text{ atm}} = 3.43 \text{ L mol}^{-1}$$

Even at these extreme conditions, the molar volume is still large, a characteristic of a gas. It is, however, smaller than that at STP, 22.4 L mol^{-1}.

5.34 The tungsten vapor can be treated as an ideal gas. The molar volume equals to volume of a sample divided by the number of moles present. Then:

$$\frac{V}{n} = \frac{RT}{P} = \frac{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})2773 \text{ K}}{7.0 \times 10^{-9} \text{ atm}} = 3.25 \times 10^{10} \text{ L mol}^{-1}$$

If the vapors occupy 3.25×10^{10} L per mole they contain 1 mol per 3.25×10^{10} L. But a mole of tungsten is 6.022×10^{23} atoms so there are 1.9×10^{13} atoms per liter, or 1.9×10^{10} per cm^3.

5.36 The partial pressure of the hydrogen is the total pressure minus the vapor pressure of water at this temperature, that is

$$P_{H_2} = P_{tot} - P_{H_2O} = 0.9900 - 0.0313 = 0.9587 \text{ atm}$$

The chemical amount of hydrogen in a 1.000 L sample of the wet hydrogen is

$$n_{H_2} = \frac{PV}{RT} = \frac{(0.9587 \text{ atm})(1.000 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(298.15 \text{ K})} = 0.039185 \text{ mol H}_2$$

The mass of hydrogen is this chemical amount multiplied by 2.01588 g mol^{-1}, the molar mass of H_2. The answer is 0.07899 g of H_2.

5.38 The chemical amount of the ammonia that is produced can be determined from the stoichiometry of the balanced equation

$$3.68 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.491 \text{ g NH}_4\text{Cl}} \times \frac{1 \text{ mol NH}_3}{1 \text{ g NH}_4\text{Cl}} = 0.06880 \text{ mol NH}_3$$

This amount of ammonia exerts a partial pressure of 0.9465 atm in the mixture; the water vapor exerts the other 0.0419 atm. According to Dalton's law the water vapor and the ammonia do not interact with each other in the container but instead effectively interpenetrate. The volume of the wet ammonia therefore equals the volume that dry ammonia would occupy if present by itself. This volume is calculated using the chemical amount of ammonia and the partial pressure of ammonia in the ideal gas equation:

$$V = \frac{nRT}{P} = \frac{(0.06880 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(303.15 \text{ K})}{(0.9465 \text{ atm})} = 1.81 \text{ L}$$

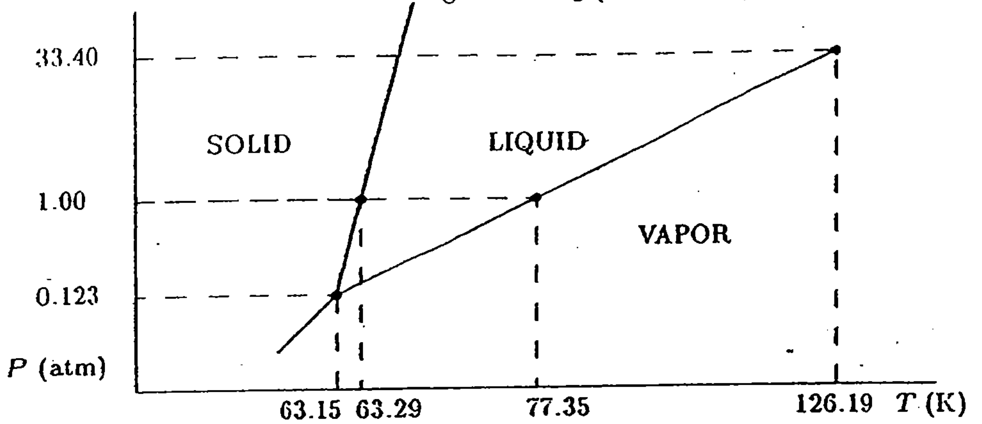
5.40 Reading from the figure across on the $P = 4$ atm line to the liquid/vapor equilibrium line and then down to the temperature axis gives an estimate of 430 K or 157°C for the boiling point of water in the pressure cooker.

5.42 The interatomic forces in aluminum are stronger because it melts and boils higher than thallium. Hence, we expect the vapor pressure of thallium to be higher than that of aluminum at room temperature.

5.44 Gray tin is favored over white tin by lower temperature, but white tin is favored by higher pressure (because it is more dense than gray tin). Suppose the two forms of tin are present at equilibrium at 1 atm and 13.2°C. Raising the pressure to 2 atm (eventually) converts all the tin to white tin. To restore the gray tin the temperature must be adjusted in the direction that favors gray tin, that is, the temperature must be lowered below 13.2°C.

5.46 The triple point and critical point are joined by a line on the *PT* graph that represents the conditions at which liquid and gaseous N_2 are in equilibrium. The normal boiling point is on this line. The line curves, but its curvature cannot be determined from the available data. The solid/liquid equilibrium line extends from the triple point to the normal melting point of nitrogen and beyond. It curves, but its slope is positive, according to the densities given in the problem. The solid/gas equilibrium line extends downward from the triple point. Solids are always more dense than gases, so the slope of this line is positive.

Phase Diagram for N_2 (not to scale)



5.48 (a) The phase diagram of H_2O (text Figure 5.21c) confirms that at equilibrium at room conditions (the starting conditions in the process described in the problem), water is a liquid.

(b) At 400 K and 1 atm, H_2O is a gas, according to the phase diagram.

(c) Although the water starts out as a liquid and ends as a gas in the process described, *no phase transition occurs*. The water is taken into the supercritical region by the changes described. The change from liquid to supercritical fluid is smooth and gradual and the subsequent change from supercritical fluid to gas is also continuous. There is no abrupt change in density or other physical properties and therefore no phase transition.

5.50 (a) The vapor pressure of solid hydrogen, and liquid hydrogen *both* equal the external pressure on the system at the triple point of hydrogen. The answer is 0.069 atm.

(b) The pressure is maintained at a value below the triple-point pressure of hydrogen. Hence the solid hydrogen converts directly to the gas; it sublimes.

5.52 The tube must contain 0.235 g of ammonia for every cm^3 of volume. If it contains more ammonia than this, the ammonia will be liquid and will become supercritical above 132.23°C without anything to be seen from the outside. If it contains less ammonia, the ammonia will be gaseous below the critical temperature and become supercritical above that temperature, again with nothing to be seen. The interior radius of the tube is $5.0 - 4.20 = 0.80 \text{ mm} = 0.080 \text{ cm}$. The height of the tube is 15.5 cm so that its volume is

$$V = \pi r^2 h = \pi\ (0.080)^2 \text{ cm}^2 \times 15.5 \text{ cm} = 0.3116 \text{ cm}^3$$

The required mass of ammonia is

$$m = dV = (0.235 \text{ g cm}^{-3}) \times (0.3116 \text{ cm}^3) = 0.0732 \text{ g}$$

5.54 The point of the problem is not the calculations, which involve mere substitution into the formula, but the large differences in the diffusive displacement of molecules in the three phases. Let Δr equal the root-mean-square displacement. Then: (a) For $O_2(g)$:

$$\Delta r = \sqrt{6D\Delta t} = \sqrt{6\ (2.1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1})\ 3600 \text{ s}} = 0.67 \text{ m}$$

(b) For $H_2O(l)$:

$$\Delta r = \sqrt{6D\Delta t} = \sqrt{6\ (2.26 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})\ 3600\ \mathrm{s}} = 0.0070\ \mathrm{m}$$

(c) For $Na(s)$:

$$\Delta r = \sqrt{6D\Delta t} = \sqrt{6\ (5.8 \times 10^{-13}\ \mathrm{m^2\,s^{-1}})\ 3600\ \mathrm{s}} = 0.00011\ \mathrm{m}$$

5.56 Compute the ratio a/b for the four substances

$$\begin{aligned} \frac{a}{b} &= \frac{1.390}{0.03913} = 35.52\ \mathrm{L\ atm\ mol^{-1}} && \text{for } N_2 \\ \frac{a}{b} &= \frac{0.2444}{0.02661} = 9.185\ \mathrm{L\ atm\ mol^{-1}} && \text{for } H_2 \\ \frac{a}{b} &= \frac{6.714}{0.05636} = 119.1\ \mathrm{L\ atm\ mol^{-1}} && \text{for } SO_2 \\ \frac{a}{b} &= \frac{3.667}{0.04081} = 89.86\ \mathrm{L\ atm\ mol^{-1}} && \text{for HCl} \end{aligned}$$

The strength of the attractive forces goes as the magnitude of a/b so the ranking is

$$SO_2 > HCl > N_2 > H_2$$

5.58 Because the density (mass per unit volume) of the water increases as it is heated from 0.0 to 4.0°, its volume per unit mass decreases. The mass of a sample is not changed by heating, so the volume of the water must decrease; the coefficient of thermal expansion is negative in this range of temperature. Positive coefficients of thermal expansion are far more common than negative ones for solids and liquids. The coefficients of thermal expansion of gases are always positive.

5.60 Assuming that the tungsten vapor is an ideal gas (a very good assumption at this exceedingly low pressure) allows computation of the molar volume:

$$\frac{V}{n} = \frac{RT}{P} = \frac{(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})(1273\ \mathrm{K})}{2 \times 10^{-25}\ \mathrm{atm}} = 5.2 \times 10^{26}\ \mathrm{L\ mol^{-1}}$$

This is the volume per mole; the volume per atom is this number divided by Avogadro's number:

$$\left(\frac{5.2 \times 10^{26}\ \mathrm{L}}{1\mathrm{mol}}\right) \times \left(\frac{1\ \mathrm{mol}}{6.022 \times 10^{23}\ \mathrm{atoms}}\right) = 9 \times 10^{2}\frac{\mathrm{L}}{\mathrm{atom}}$$

5.62 The chemical amount of air that was present in the 6.00 L portion of air mixed with the vapors of the unknown can be computed because its physical state after purification is fully described

$$n_{\mathrm{air}} = \frac{PV}{RT} = \frac{(1.000\ \mathrm{atm})(3.75\ \mathrm{L})}{(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})(223.15\ \mathrm{K})} = 0.2048\ \mathrm{mol}\ .$$

Now, compute the pressure that this chemical amount of air exerted as part of the 6.00 L mixture

$$\begin{aligned} P_{\mathrm{air}} &= \frac{n_{\mathrm{air}}RT}{V} \\ P_{\mathrm{air}} &= \frac{(0.2048\ \mathrm{mol})(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})(298.15\ \mathrm{K})}{6.00\ \mathrm{L}} = 0.835\ \mathrm{atm} \end{aligned}$$

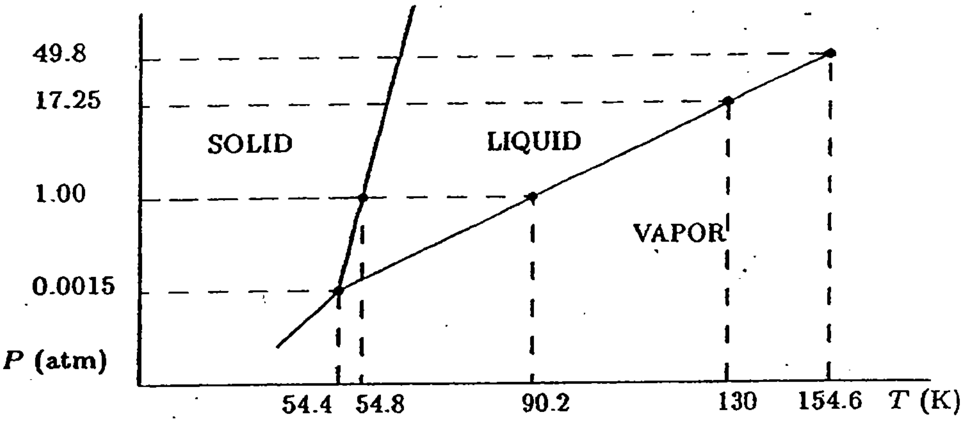
But the total pressure above the unknown was 0.980 atm. By Dalton's law

$$P_{\text{unknown}} = 0.980 - 0.835 = 0.145 \text{ atm}$$

5.64 If the pressure inside the lighter is not to exceed 1 atm, then the butane must be a gas. Pressurization is the only way to keep the butane a liquid at room temperature, because room temperature exceeds its normal boiling point. Estimating the amount of gaseous butane in a lighter with a storage volume of 10 mL requires substitution in the ideal gas equation and solving for n. The conditions are: $P = 1$ atm, $V = 0.01$ L, and $T = 298$ K. Doing the arithmetic gives $n = 4.1 \times 10^{-4}$ mol of butane which amounts to 0.024 g of butane (the $\mathcal{M}$ of butane is 58.1 g mol^{-1}). This is about 1/200 of the butane in a standard lighter.

5.66

Phase Diagram for O_2 (not to scale)



5.68 (a) A 400 atm pressure would lower the melting point of ice to about −4°C.

(b) The pressure exerted by the blade of the skate is

$$P = \frac{F}{A} = \frac{ma}{A} = \frac{(75 \text{ kg})\,(9.8 \text{ m s}^{-2})}{8.0 \times 10^{-5} \text{ m}^2} = 9.2 \times 10^6 \text{ Pa}$$

This pressure equals about 90 atm. Therefore, ice at −5°C does not melt under the pressure of the blade.

5.70 HBr has stronger attractive forces than HCl because of its larger molar mass. HF also has stronger attractive forces but for a different reason: it forms hydrogen bonds. Stronger forces drive up the characteristic temperature to form a gas from a liquid.

5.72 Let us take $1/2(3.4 \times 10^{-10}$ m) as the radius of an argon atom, because (3.4×10^{-10} m) is the distance where the interaction potential for a *pair* of atoms changes from repulsive to attractive. The volume of one argon atom is then

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(1.7 \times 10^{-10} \text{ m})^3 = 2.06 \times 10^{-29} \text{ m}^3$$

The volume filled by one mole of argon atoms is Avogadro's number times this

$$V = (6.022 \times 10^{23})(2.06 \times 10^{-29} \text{ m}^3) = 1.24 \times 10^{-5} \text{ m}^3$$

The fractional volume occupied is then

$$\frac{1.25 \times 10^{-5}\ \mathrm{m}^3}{(24.0\ \mathrm{L})(10^{-3}\ \mathrm{m}^3\ \mathrm{L}^{-1})} = 5.2 \times 10^{-4}$$