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 answer is discussed on text page 7 with respect to salt / 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 requires finding a method, any one method, that successfully breaks it down into simpler substances. Proving that a material *is* an element requires the proof of a negative: that there is no way to break it down. Mistaken reports of new elements arise when a compound or mixture resists breakdown by all of the methods tried but subsequently proves decomposable by new methods.

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

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

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

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

The compound may of course contain other elements.

1.8 **a)** The mass of fluorine that combines with 1.0000 g of iodine in these compounds is the mass percentage of fluorine divided by the mass percentage of iodine. This is well shown 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. 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**, calculate the masses of chlorine per gram of tungsten in the four compounds:

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 mass of chlorine are

0.3856/0.3856 = 1.0000 = 2 : 2 0.7715/0.3856 = 2.0008 = 4 : 2

0.9643/0.3856 = 2.5008 = 5 : 2 1.1570/0.3856 = 3.0005 =6 : 2

The formulas are WCl_2, WCl_4, WCl_5, and WCl_6.

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

$$2\mathrm{CH_3OH}(g) + 3\mathrm{O_2}(g) \rightarrow 2\mathrm{CO_2}(g) + 4\mathrm{H_2O}(g)$$

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 (and under the assumption that the reaction goes to completion as written).

1.16 The atomic mass of naturally occurring neon is found by multiplying each isotope's fractional abundance by its mass and summing over all the isotopes

$$A = A_1p_1 + A_2p_2 + \cdots + A_np_n$$
$$A_{\mathrm{Ne}} = (0.9000)(19.99212) + (0.0027)(20.99316) + (0.0973)(21.99132) = 20.19$$

1.18 This problem resembles problem **1.16**, except that the atomic mass of one of the five isotopes of Zr is not known and the weighted-average atomic mass of natural zirconium (91.224) is known. Obtain the natural abundance of the isotope of interest by subtraction

$$p(^{90}\mathrm{Zr}) = 1 - 0.1127 - 0.1717 - 0.1733 - 0.0278 = 0.5145$$

Let the relative mass of this isotope be A_{90}. Then

$$91.224 = 0.5145A_{90} + 0.1127(90.9056) + 0.1717(91.9050) + 0.1733(93.9063) + 0.0278(95.9083)$$
$$A_{90} = 89.91$$

1.20 **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.

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

1.24 **a)** As suggested in the hint, look at *differences* in charge. List the droplets in order of increasing charge and compute the amount by which each differs in charge from its predecessor

Droplet No.	Charge/10^{-19} C	Difference/10^{-19} C	No. e^- on droplet
1	6.563	—	4
2	8.204	1.641	5
3	11.50	3.296	7
4	13.13	1.63	8
5	16.48	3.35	10
6	18.08	1.60	11
7	19.71	1.63	12
8	22.89	3.18	14
9	26.18	3.29	16

Moving down the list, the charges on the droplets increase by either 1 or 2 times 1.64×10^{-19} C. This suggests that a fundamental unit of charge exists and is approximately equal to 1.64×10^{-19} C. Dividing this quantity into the nine observed charges gives results that are all very close to whole numbers. Take these whole numbers to equal the number of the fundamental units of charge (electrons) on each droplet.

b) Divide the observed charge on each droplet by the apparent number of electrons on that droplet (that is, divide column 2 by column 4 in the preceding):

1. 1.6407×10^{-19}C
2. 1.6408×10^{-19}C
3. 1.6429×10^{-19}C
4. 1.6413×10^{-19}C
5. 1.6480×10^{-19}C
6. 1.6436×10^{-19}C
7. 1.6425×10^{-19}C
8. 1.6350×10^{-19}C
9. 1.6363×10^{-19}C

The average of the nine values is 1.641×10^{-19}C.

c) In the preceding, the least difference among the charges on the nine droplets has been taken as the "quantum of electrical charge." The actual quantum of charge however might be some fraction ($\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$, etc.) of this value. One can confirm that 1.641×10^{-19}C is truly the charge on a single electron only by extensive search for droplets having lesser charge.

1.26

$$\text{Density of neutron star} = \frac{\text{mass}}{\text{volume}} = \frac{6.0\times10^{56}\times1.675\times10^{-24}\,\text{g}}{\left(\frac{4}{3}\right)\pi\left(20\times10^{5}\,\text{cm}\right)^{3}} = 3.0\times10^{13}\,\text{g cm}^{-3}$$

$$\text{Mass of }^{232}\text{Th nucleus} = 142\left(1.675\times10^{-24}\ \text{kg}\right)+90\left(1.673\times10^{-24}\ \text{g}\right) = 3.884\times10^{-22}\ \text{g}$$

$$\text{Density of }^{232}\text{Th nucleus} = \frac{3.884\times10^{-22}\,\text{g}}{\left(\frac{4}{3}\right)\pi\left(9.1\times10^{-13}\,\text{cm}\right)^{3}} = 1.2\times10^{14}\,\text{g cm}^{-3}$$

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

1.28 Let A_1 be the *fractional* abundance of ^{85}Rb and let A_2 be the fractional abundance of ^{87}Rb.

Then

$$A_1\,(84.9117) + A_2(86.9092) = 85.4678 \text{ and } A_1 + A_2 = 1$$

Solving gives A_1 = 0.7216. The percentage of ^{85}Rb is 72.16%; ^{87}Rb is 27.84%.

Chapter 2

Chemical Formulas, Chemical Equations, and Reaction Yields

2.2 Avogadro's number of ^{12}C atoms has a mass of exactly 12 g. By use of the ratio given in the problem, Avogadro's number of F atoms must have a mass of 18.998403 g. For 100 million atoms of fluorine

$$m_F = 10^8 \text{atoms F} \times \left(\frac{18.998403 \text{ g F}}{6.0221420 \times 10^{23} \text{atom F}} \right) = 3.1547584 \times 10^{-15} \text{g F}$$

2.4 The problem is about handling the nesting of parentheses in chemical formulas when computing molecular masses, formula masses, and molar masses. The answers: **a)** 177.382; **b)** 598.156; **c)** 254.2; **d)** 98.079; **e)** 450.446. These are relative masses and so have no units.

2.6 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 $\left(6.022 \times 10^{23}\right)\left(2.88 \times 10^{-10} \text{m}\right) = 1.73 \times 10^{14} \text{m}$.

2.8 Express the amounts of each sample in the same unit of mass. In the case of the SF_4, convert from the given number of moles to grams using the molar mass. In the cases of the Cl_2O_7 and Ar, convert from the given number of particles to chemical amount and from there to mass. The amount of CH_4 is already in grams. The results are

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

2.10

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

The cost to three significant figures is \$2 480.

2.12

$$N_{Si} = 415 \text{cm}^3 \times \frac{0.00278 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol } Si_2H_6}{62.219 \text{ g } Si_2H_6} \times \frac{6.022 \times 10^{23} \text{ molecule } Si_2H_6}{1 \text{ mol } Si_2H_6}$$
$$\times \frac{2 \text{ atoms Si}}{1 \text{ molecule Si}} = 2.23 \times 10^{22} \text{atom Si}$$

2.14 Find the mass fractions by dividing the mass of each element present in a mole of acetaminophen (N-acetyl-*p*-aminophenol, $C_8H_9NO_2$) by the molar mass

$$f_C = \frac{8\times 12.011 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} = 0.6356 \qquad f_H = \frac{9\times 1.00794 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} = 0.06001$$

$$f_N = \frac{1\times 14.0067 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} = 0.09266 \qquad f_O = \frac{2\times 15.9994 \text{ g mol}^{-1}}{151.165 \text{ g mol}^{-1}} = 0.2117$$

The mass percentages equal the mass fractions multiplied by 100%.

2.16 Save work by *estimating* the fluorine content of each compound. Thus, HF is certainly the compound richest in fluorine by mass because the only other atom in its formula 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 × 12)/5 ≈ 14; in BrF it is 79.9; in UF_6 it is 238/6 ≈ 40. The desired order is therefore BrF < UF_6 < C_6HF_5 < HF.

2.18 The pharmacist mixes 286 g of Na_2CO_3 with 150 g of $C_2H_5NO_2$, using water as a mixing agent. After all the water is driven away, the mixture weighs 436 g. The mass of carbon from the Na_2CO_3 is (12.011/105.988) × 286 g; the mass of carbon from the $C_2H_5NO_2$ is (2 × 12.011/75.067) × 150 g where the 105.988 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 80.412 g. The mass percentage of carbon is this mass divided by 436 g and multiplied by 100%. It is 18.4%.

2.20 Imagine 100.0 g of bromoform. The mass of bromine 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 1.18705 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 2.99 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.

2.22 Imagine 100.0000 g of the compound. This sample contains 1.6907 g of O and 98.3093 g of Cs. The chemical amount of oxygen 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.

2.24 The empirical formulas of the five compounds are

A. CO_2, B. CO_1, C. C_4O_3, D. C_3O_2, E. C_5O_2

All five of these compositions exist. The first two are well-known. The third is mellitic anhydride (molecular formula $C_{12}O_9$). The last two are carbon suboxides having molecular formulas identical to their empirical formulas.

2.26 Compare the chemical amounts of the three elements in the compounds

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

$$n_C = n_{CO_2} = \frac{1.876 \text{ g}}{44.010 \text{ g mol}^{-1}} = 0.04263 \text{ mol}$$

$$n_N = n_{NO_2} = \frac{3.921 \text{ g}}{46.0055 \text{ g mol}^{-1}} = 0.08523 \text{ mol}$$

Divide each of these amounts by the smallest. The resulting ratios are 1 : 1.001 : 2.001. This means that the empirical formula is $CaCN_2$

2.28 Two gases held at the same conditions contain the same number of molecules per unit volume. This means that the ratio of molar masses of these two gases equals the ratio of their densities:

$$\frac{\mathcal{M}_{P_n}}{\mathcal{M}_{N_2}} = \frac{2.7\ \text{g L}^{-1}}{0.62\ \text{g L}^{-1}} \text{ hence } \mathcal{M}_{P_n} = \left(\frac{2.7}{0.62}\right)\left(28.014\ \text{g mol}^{-1}\right) = 1.2\times10^{2}\ \text{g mol}^{-1}$$

The molar mass of atomic P is only 30.97 g mol^{-1}. The P_4 molecule however has a molar mass of 124 g mol^{-1}, which equals 1.2 × 10^2 g mol^{-1} within the precision of the data (two significant digits). Conclude that there are four P atoms per molecule under these conditions.

2.30 **a)** The relative molecular mass of the binary compound is (2.53) (28.013) = 70.9.

b) Each molecule of the compound has one N atom because

$$\frac{8.21\ \text{g}}{70.9\ \text{g mol}^{-1}} = 0.116\ \text{ mol compound contains } \frac{1.62\ \text{g}}{14.007\ \text{g mol}^{-1}} = 0.116\ \text{mol N}$$

c) The maximum possible value of the relative atomic mass of the other element is 70.9 – 14.0 = 56.9.

d) Divide 56.9 by the positive integers: 56.9/2 = 28.5; 56.9/3 = 19.0; 56.9/4 = 24.2, and so forth. Compare the results to the known relative atomic masses. The closet fit is F (relative atomic mass 19.0).

e) NF_3

2.32 **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) $NaBH_4 + 2\,H_2O \rightarrow NaBO_2 + 4\,H_2$

2.34 **a)**

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

b)

$$m_{CO_2} = \left(\frac{1.000\ \text{g C}_3\text{H}_8}{44.096\ \text{g mol}^{-1}}\right)\left(\frac{3\,\text{mol CO}_2}{1\ \text{mol C}_3\text{H}_8}\right)\times 44.010\ \text{g mol}^{-1} = 2.994\ \text{g}$$

c)

$$m_{Mg_2P_2O_7} = \left(\frac{1.000\ \text{g MgNH}_4\text{PO}_4}{137.315\ \text{g mol}^{-1}}\right)\left(\frac{1\ \text{mol Mg}_2\text{P}_2\text{O}_7}{2\ \text{mol MgNH}_4\text{PO}_4}\right)\times 222.55\ \text{g mol}^{-1} = 0.8104\ \text{g}$$

2.36 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

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

2.38 Use the balanced equation $\text{Si}_4\text{H}_{10} + \frac{13}{2}\text{O}_2 \rightarrow 4\text{SiO}_2 + 5\text{H}_2\text{O}$

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

2.40

$$m_{\text{CS}_2} = 67.2 \text{ g S} \times \frac{1 \text{ mol S}}{32.066 \text{ g S}} \times \frac{1 \text{ mol CS}_2}{4 \text{ mol S}} \times \frac{76.143 \text{ g CS}_2}{1 \text{ mol CS}_2} = 39.9 \text{ g CS}_2$$

2.42

$$m_{\text{Ca}_3(\text{PO}_4)_2} = 69.8 \text{ g P}_4 \times \frac{1 \text{ mol}}{123.895 \text{ g}} \times \frac{2 \text{ mol Ca}^3(\text{PO}_4)_2}{1 \text{ mol P}_4} \times \frac{310.18 \text{ g}}{1 \text{ mol}} = 349 \text{ g Ca}_3(\text{PO}_4)_2$$
$$m_{\text{CaSiO}_3} = 69.8 \text{ g P}_4 \times \frac{1 \text{ mol}}{123.895 \text{ g}} \times \frac{6 \text{ mol CaSiO}_3}{1 \text{ mol P}_4} \times \frac{116.16 \text{ g}}{1 \text{ mol}} = 393 \text{ g CaSiO}_3$$

2.44 **a)** Let $\mathcal{M}_A$ represent the molar mass of element A. Then $\mathcal{M}_A$ + 3(126.90) g mol^{-1} is the molar mass of AI3 and $\mathcal{M}_A$ + 3(35.453) g mol^{-1} is the molar mass of ACl_3. Use the stoichiometry of the equation to express the mass of ACl_3 obtained in terms of the mass of AI_3 treated

$$0.3776 \text{ g} = 0.8000 \text{ g AI}_3 \times \frac{1 \text{ mol AI}_3}{(\mathcal{M}_A + 380.7)\text{g AI}_3} \times \frac{1 \text{ mol ACl}_3}{1 \text{ mol AI}_3} \times \frac{(\mathcal{M}_A + 106.36)\text{g ACl}_3}{1 \text{ mol ACI}_3}$$

Which becomes

$$0.8000(\mathcal{M}_A + 106.36) = 0.3776(\mathcal{M}_A + 380.7) \quad \text{from which} \quad \mathcal{M}_A = 138.9 \text{ g mol}^{-1}$$

b) The element is lanthanum, La.

2.46 Express the amount of hydrogen that is evolved as a chemical amount

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

Let the mass of iron in the original mixture be represented by *x*. Then

$$n_{\text{Fe}} = \frac{x \text{ g Fe}}{55.845 \text{ g mol}^{-1}} \quad \text{and} \quad n_{\text{Al}} = \frac{(9.62 - x)\text{g Al}}{26.982 \text{ g mol}^{-1}}$$

The 0.366 mol of H_2 is evolved by these molar amounts of Fe and Al in reaction with excess HCl according to the equations given in the problem. Determine the molar amount of H_2 that each metal produces and add them

$$\frac{x \text{ g Fe}}{55.845 \text{ g mol}^{-1}}\left(\frac{1 \text{ mol H}_2}{1 \text{ mol Fe}}\right)+\frac{(9.62-x) \text{ g Al}}{26.982 \text{ g mol}^{-1}}\left(\frac{3 \text{ mol H}_2}{2 \text{ mol Al}}\right)=0.366 \text{ mol H}_2$$

$$-0.03769\,x+0.5348=0.366 \quad \text{from which } x=4.48 \text{ g Fe}$$

2.48 **a)** $NH_3 + CH_4 \rightarrow HCN + 3\ H_2$

b) The reaction system contains 700.0 g at the start, distributed as follows

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

NH_3 is the limiting reactant. After the reaction goes to completion the system contains

$$m_{\text{HCN}}=11.74 \text{ mol NH}_3\times\frac{1 \text{ mol HCN}}{1 \text{ mol NH}_3}\times\frac{27.026 \text{ g}}{\text{mol HCN}}=317.3 \text{ g HCN}$$

$$m_{\text{H}_2}=11.74 \text{ mol NH}_3\times\frac{3 \text{ mol H}_2}{1 \text{ mol NH}_3}\times\frac{2.0158 \text{ g}}{\text{mol H}_2}=71.0 \text{ g H}_2$$

$$m_{\text{CH}_4}=(31.17-11.74 \text{ mol CH}_4)\times\frac{16.043 \text{ g}}{\text{mol CH}_4}=311.7 \text{ g CH}_4$$

The sum of these three masses is 700.0 g, the same total mass as before the reaction.

2.50 The theoretical yield of $TiCl_4$ is

$$m_{\text{TiCl}_4}=7.39 \text{ kg TiO}_2\times\frac{1 \text{ kmol TiO}_2}{79.88 \text{ kg TiO}_2}\times\frac{1 \text{ kmol TiCl}_4}{1 \text{ kmol TiCl}_2}\times\frac{189.69 \text{ kg TiCl}_4}{1 \text{ kmol TiCl}_4}=17.55 \text{ kg}$$

The percentage yield is 14.24 kg/17.55 kg × 100% = 81.1%.

2.52 Do the calculations to five significant figures, the precision of the tabulated atomic mass of tungsten. There is 0.43134 mol of W in a 100.000 g sample of the white oxide, and 1.29395 mol of O. The ratio of these numbers is 2.9998—the empirical formula is WO_3. 100.000 g of the blue oxide contains 0.43975 mol W and 1.19709 mol of O. The ratio of these two amounts is 2.7222. 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.

2.54 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 subscripts are whole numbers, but they are hardly small whole numbers.

2.56 The empirical formula of the compound is BCl based on

$$n_{\mathrm{B}} = \frac{0.664 \text{ g B}}{10.811 \text{ g mol}^{-1}} = 0.0614 \text{ mol B} \quad n_{\mathrm{Cl}} = \frac{(2.842 \text{ g} - 0.664 \text{ g})\mathrm{Cl}}{35.453 \text{ g mol}^{-1}} = 0.0614 \text{ mol Cl}$$

To obtain the molecular formula, write

$$n_{\mathrm{Cl_2}} = 0.0614 \text{ mol Cl} \times \left(\frac{1 \text{ mol Cl}_2}{2 \text{ mol Cl}} \right) = 0.0307 \text{ mol Cl}_2$$

From Avogadro's hypothesis, the chemical amount of the gaseous compound in the original sample was

$$n_{\text{compound}} = 0.0307 \text{ mol Cl}_2 \times \left(\frac{0.153 \text{ L compound}}{0.688 \text{ L Cl}_2} \right) = 0.00683 \text{ mol compound}$$

This allows computation of the molar mass

$$\mathcal{M}_{\text{compound}} = \frac{2.842 \text{ g}}{0.00683 \text{ mol}} = 416.3 \text{ g mol}^{-1}$$

The molar mass corresponding to the empirical formula BCl is only 46.264 g mol^{-1}. The ratio 416.3/46.264 equals 9.00, so the molecular formula is B_9Cl_9.

2.58 The balanced chemical equation reads

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

The right-hand side of the equation is short 9 atom of C, which must be part of the phenylalanine molecule. Balancing amounts of H, N and O in the same way establishes the molecular formula of phenylalanine to be $C_9H_{11}NO_2$.

2.60 Assume that all the carbon is evolved as CH_4. Then 1 mol Al_4C_3 generates 3 mol CH_4

$$m_{\mathrm{CH_4}} = \frac{63.2 \text{ g Al}_4\text{C}_3}{143.96 \text{ g mol}^{-1}} \times \frac{3 \text{ mol CH}_4}{1 \text{ mol Al}_4\text{C}_3} \times \frac{16.043 \text{ g CH}_4}{1 \text{ mol CH}_4} = 21.1 \text{ g}$$

2.62 Let x represent the mass of $SrCO_3$ in the sample. Then $0.800 - x$ is the mass of $BaCO_3$.

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

$$\text{and} \quad n_{\mathrm{CO_2}} = \frac{0.211 \text{ g CO}_2}{44.010 \text{ g mol}^{-1}} = 0.004794 \text{ mol}$$

Each mole of $SrCO_3$ and $BaCO_3$ generates one mole of CO_2. This means

$$\left(\frac{x}{147.63} + \frac{0.800 - x}{197.34} \right) \text{mol} = 0.004794 \text{ mol} \quad \text{which gives} \quad x = 0.434 \text{ g}$$

The percentage of $SrCO_3$ in the sample was 0.434 g/0.800 g × 100% = 54.2%.

2.64 Assume that your car gets 20 miles per U.S. gallon. Then reducing driving by 20 miles per week would save you 1 gallon a week, or 52 gallons a year. In the metric system this is

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

Gasoline floats on water, so its density is less than the density of water (which is 1.0 g cm^{-3}). Take the density of gasoline to be 0.9 g cm^{-3}, or 0.9 kg L^{-1}. Your annual savings is then about 180 kg of gasoline. Approximate the chemical formula of gasoline as C_8H_{18} (octane). Then

$$n_{\text{gasoline}} \approx 180 \times 10^3 \text{g } C_8H_{18} \times \left(\frac{1 \text{ mol}}{114.2 \text{ g } C_8H_{18}} \right) = 1.6 \times 10^3 \text{ mol}$$

Combustion of octane release 8 mol of CO_2 per mole. The mass of CO_2 not released is

$$m_{CO_2} \approx 1.6 \times 10^3 \text{mol } C_8H_{18} \times \left(\frac{8 \text{ mol } CO_2}{1 \text{ mol } C_8H_{18}} \right) \times \left(\frac{44 \text{ g } CO_2}{1 \text{ mol } CO_2} \right) = 5.7 \times 10^5 \text{ g} \approx 570 \text{ kg}$$

$$\approx 570 \text{ kg} \left(\frac{1 \text{ lb}}{0.4536 \text{ kg}} \right) = 1300 \text{ lb } CO_2$$

This is on the order of 1000 pounds, the amount that is mentioned in the problem. If your car gets 30 miles per gallon, then the same weekly 20 mile cut in its use would reduce your CO_2 emissions by 2/3 of 1300 pounds.

2.66 Compute the theoretical yield of $KClO_4$ for comparison to the observed yield of 3.00 g. Balance the chemical equation: 4 $KClO_3(s)$ $\rightarrow$ 3 $KC1O_4(s)$ +KCl(s). Then

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

$$= 3.392 \text{ g } KClO_4$$

The percentage yield is (3.00/3.392) × 100% = 88.4%.

2.68 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)

$$m_{Si} = 125 \text{ g } Si_3N_4 \text{ isolated} \times \left(\frac{100 \text{ g } Si_3N_4 \text{ formed}}{95.0 \text{ g } Si_3N_4 \text{ isolated}} \right) \times \left(\frac{1 \text{ mol } Si_3N_4}{140.285 \text{ g } Si_3N_4 \text{ formed}} \right)$$

$$\times \left(\frac{3 \text{ mol Si}}{1 \text{ mol } Si_3N_4} \right) \times \left(\frac{28.086 \text{ g Si}}{1 \text{ mol Si}} \right) = 79.0 \text{ g Si}$$

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	

No obvious reason exists to treat horizontal trends in the table as more or less important than vertical trends. Hence, just average the four melting points to get a predicted melting point. 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)** Use Coulomb's law (text equation 3.1). Assume that the distance between the electron and the gold nucleus is *exactly* 2 Å (2×10^{-10} m), and carry out the arithmetic to three significant digits

$$F(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} = \frac{(-e)(+79\ e)}{4\pi\epsilon_0 r^2}$$

$$= \frac{-79(1.602\times10^{-19}\ \mathrm{C})^2}{4\pi(8.854\times10^{-12}\ \mathrm{C^2J^{-1}m^{-1}})(2.00\times10^{-10}\mathrm{m})^2} = -4.56\times10^{-7}\ \mathrm{N}$$

b) Again, assume that the distance between the two particles is *exactly* 2 Å and carry out the arithmetic to three significant digits

$$V(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r} = \frac{-(e)(79\ e)}{4\pi\epsilon_0 r}$$

$$= \frac{-(79)(1.602\times10^{-19}\ \text{C})^2}{4\pi(8.854\times10^{-12}\ \text{C}^2\ \text{J}^{-1}\ \text{m}^{-1})(2\times10^{-10}\ \text{m})} = -9.11\times10^{-17}\ \text{J}$$

3.8 Picture the helium nucleus as speeding along in a straight liane aimed directly at the gold nucleus, which is motionless. At the moment that it is 1 Å away, it experiences an electrostatic (Coulombic) force F_1, has Coulombic potential energy V_1, and has velocity v_1. At the moment that it is 0.5 Å away, it experiences force F_2, has potential energy V_2, and has velocity v_2.

a) The change in the force acting on the helium nucleus equals the final force minus the initial

$$\Delta F = F_2 - F_1 = \frac{q_{\text{Au}^{79+}} q_{\text{He}^{2+}}}{4\pi\ \epsilon_0}\left(\frac{1}{r_2^2} - \frac{1}{r_1^2}\right)$$

$$= \frac{(79)(2)(1.602\times10^{-19}\text{C})^2}{4\pi(8.854\times10^{-12}\text{C}^2\ \text{J}^{-1}\ \text{m}^{-1})}\left(\frac{1}{(1.000\times10^{-10}\text{m})^2} - \frac{1}{(2.000\times10^{-10}\text{m})^2}\right)$$

$$= (3.644\times10^{-26}\text{J m})(1.000\times10^{20}\text{m}^{-2} - 0.25000\times10^{20}\ \text{m}^{-2})$$

$$= 2.733\times10^{-6}\ \text{N}$$

b) The change in the Coulomb potential energy equals the final minus the initial value

$$\Delta V = \frac{q_{\text{Au}^{79}} + q_{\text{He}^{2+}}}{4\pi\epsilon_0}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

$$= \frac{(79)(2)(1.602\times10^{-19}\text{C})^2}{4\pi(8.854\times10^{-12}\text{C}^2\ \text{J}^{-1}\ \text{m}^{-1})}\left(\frac{1}{(1.000\times10^{-10}\ \text{m})} - \frac{1}{(2.000\times10^{-10}\ \text{m})}\right)$$

$$= (3.644\times10^{-26}\ \text{J m})(1.000\times10^{10}\text{m}^{-1} - 0.5000\times10^{10}\text{m}^{-1})$$

$$= 1.822\times10^{-16}\ \text{J}$$

c) The total energy of the system E equals the sum of its kinetic energy T and potential energy V. E is constant (conservation of energy), so

$$\Delta E = 0 = \Delta V + \Delta T$$

The gold nucleus is motionless; the kinetic energy of the system comes entirely from the motion of the helium nucleus. Then

$$\Delta \mathcal{T}_{\text{He}^{2+}} = \Delta\mathcal{T} = -\Delta V = -1.822\times10^{-16}\ \text{J}$$

Substituting for the change in the kinetic energy of the helium nucleus gives

$$\begin{aligned}
\tfrac{1}{2} m_{\mathrm{He}^{2+}} \Delta\left(v^2\right) &= -1.822 \times 10^{-16}\ \mathrm{J} \\
\Delta\left(v^2\right) &= \frac{2\left(-1.822 \times 10^{-16}\ \mathrm{J}\right)}{6.646 \times 10^{-27}\ \mathrm{kg}} \\
\left(v_2\right)^2 - \left(v_1\right)^2 &= -5.477 \times 10^{10}\ \mathrm{m^2 s^{-2}} \\
\left(v_2 - v_1\right)\left(v_2 + v_1\right) &= -5.477 \times 10^{10}\ \mathrm{m^2 s^{-2}}
\end{aligned}$$

Obtaining $\Delta v = \left(v_2 - v_1\right)$ requires additional information.

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

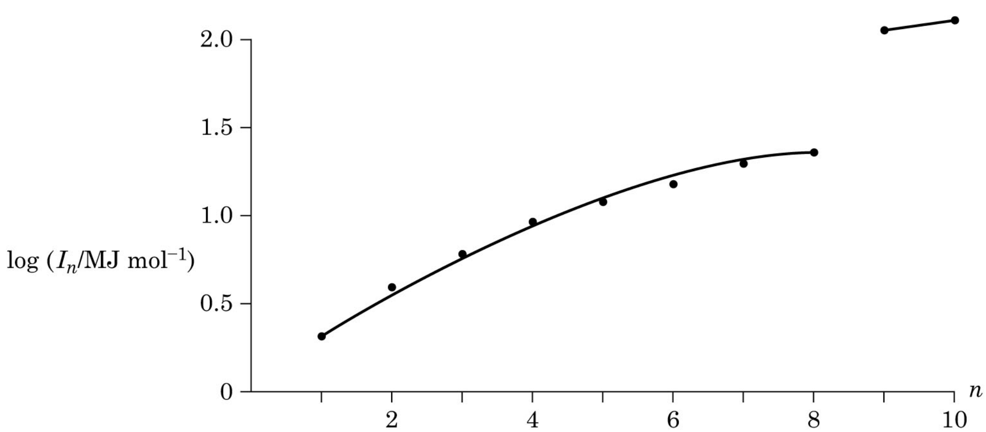
b) Selenium (Se) should have a higher IE_1 than Te; the two are in the same group and Se is higher up the periodic table.

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.

3.12 For Ne, data from text Table 3.1 give

n	I_n / MJ mol^{-1}	$\log\left(I_n / \text{MJ mol}^{-1}\right)$	n	I_n / MJ mol^{-1}	$\log\left(I_n / \text{MJ mol}^{-1}\right)$
1	2.08	0.318	6	15.24	1.183
2	3.95	0.597	7	20.00	1.301
3	6.12	0.787	8	23.07	1.363
4	9.37	0.972	9	115.38	2.062
5	12.18	1.086	10	131.43	2.119



The graph shows a slowly increasing trend for n = 1 through n = 8 followed by an abrupt increase at n = 9. This suggests an outer shell of 8 electrons outside of a very stable inner shell of 2 electrons.

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

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

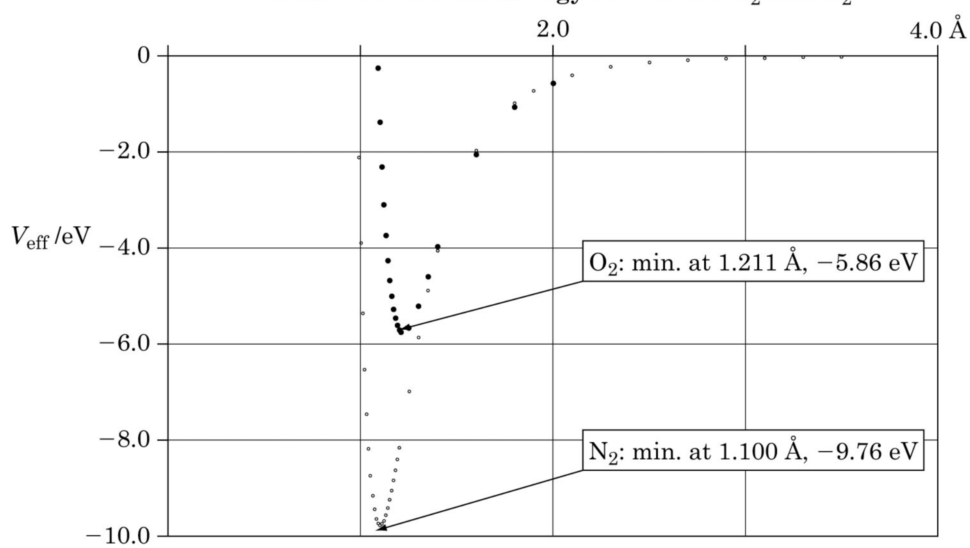
3.16 In < Sb < Se < S < Cl. The general trend is that electronegativity increases moving up a column (group) in the periodic table and moving from left to right across the groups from I toward VIII. Thus, electronegativity generally increases in a diagonal direction from lower left to upper right in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

3.18 Convert the bond energies from kJ mol^{-1} to eV, as suggested in the problem

$$N_2: \; 942 \text{ KJ mol}^{-1} \frac{0.010364 \text{ eV}}{1 \text{ kJ mol}^{-1}} = 9.76 \text{ eV} \quad O_2: \; 565 \text{ kJ mol}^{-1} \frac{0.010364 \text{ eV}}{1 \text{ kJ mol}^{-1}} = 5.86 \text{ eV}$$

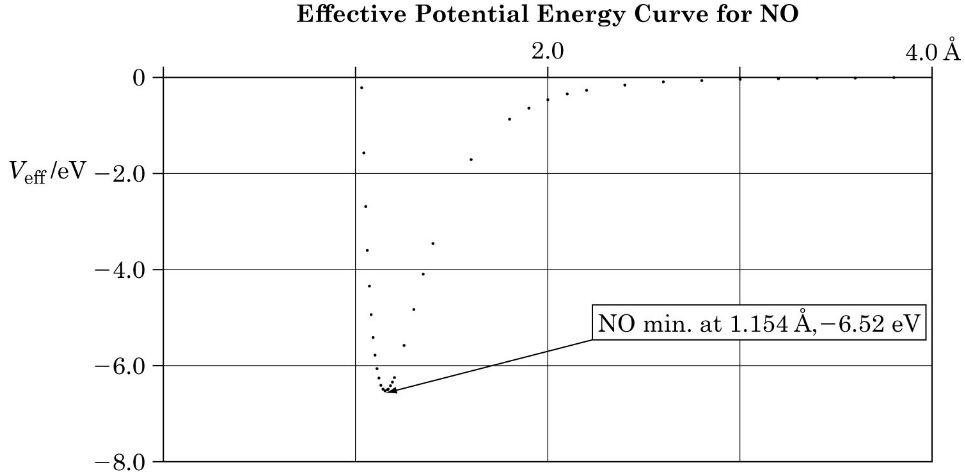
A plot of V_{eff} as a function of the interatomic distance in N_2 must have a minimum of −9.76 eV at 1.100 Å. A similar plot for O_2 must have a minimum of −5.86 eV at 1.211 Å.

Effective Potential Energy Curves for N_2 and O_2



3.20 Use the same scale that was used in problem **3.18**

Effective Potential Energy Curve for NO



The bond distance and bond energy in NO are intermediate between the bond distances and bond energies in N_2 and O_2. N_2 has a triple bond; O_2 has a double bond. Presumably NO has a bond of fractional order between 2 and 3 such as a $2\frac{1}{2}$ bond.

3.22 **a)** $\left(\text{Ra}\right)^{2+}$ 86 e^{-}'s$\left(0\text{ valence, }86\text{ core}\right)$

b) $:\ddot{\underset{..}{\text{Br}}}\cdot$ 35 e^{-}'s$\left(7\text{ valence, }28\text{ core}\right)$

c) $\left(:\ddot{\underset{..}{\text{Bi}}}\cdot\right)^{2-}$ 85 e^{-}'s$\left(7\text{ valence,}78\text{ core}\right)$

d) $\left(\cdot\text{Ga}\cdot\right)^{+}$ 30 e^{-}'s$\left(2\text{ valence, }28\text{ core}\right)$

3.24 **a)** The ΔE of the first reaction is the ionization energy of Na(g) minus the EA (electron affinity) of I(g). This quantity is defined as ΔE_∞ on text page 95. Taking data from text Figure 3.4 and Tables 3.1 and 3.2 and (mainly) Appendix F gives

$$\Delta E_\infty = 496\text{ kJ mol}^{-1} - 295\text{ kJ mol}^{-1} = 201\text{ kJ mol}^{-1}$$

The ΔE of the second reaction is the IE of I(g) minus the electron affinity of Na(g). It is ΔE_∞ for the transfer of the electron in the reverse direction

$$\Delta E_\infty = 1008\text{ kJ mol}^{-1} - 53\text{ kJ mol}^{-1} = 955\text{ kJ mol}^{-1}$$

b) Similar combination of the ionization energies and electron affinities of Rb and Br gives ΔE_∞ of the first reaction as 78 kJ mol^{-1} and ΔE_∞ of the second reaction as 1093 kJ mol^{-1}.

Even if $Na^{-1}I^{+}\left(g\right)$ and $Rb^{-}Br^{+}\left(g\right)$ were to form, the reactions transferring electrons to form $Na^{+}I^{-}$(g) and $Rb^{+}Br^{-}$(g) would be strongly favored energetically.

3.26 The process RbF(g) → Rb(g) + F(g) is the sum of these three steps

$$\begin{array}{lll}
\text{RbF}(g) & \rightarrow \ \text{Rb}+(g)+\text{F}^{-}(g) & \Delta \text{E}_1 \\
\text{Rb}^{+}(g)+e^{-} & \rightarrow \ \text{Rb}(g) & \Delta E = -IE_1(\text{Rb}) \\
\text{F}^{-}(g) & \rightarrow \ \text{F}(g)+e^{-} & \Delta E = EA(F) \\
\hline
\text{Total RbF}(g) & \rightarrow \ \text{Rb}(g)+\text{F}(g) & \Delta E_{\text{total}}
\end{array}$$

Estimate the energy change for the first step by taking the Rb-to-F bond to be ionic. The energy to separate a Rb^{+} ion and an F^{-} ion that are initially 2.274×10^{-10} m apart is

$$\Delta E_1 = \frac{e^2}{4\pi \epsilon_0 R} = \frac{(1.602\times10^{-19}\text{C})^2\left(6.022\times10^{23}\text{mol}^{-1}\right)}{4\pi\left(8.854\times10^{-12}\ \text{C}^2\ \text{J}^{-1}\ \text{m}^{-1}\right)\left(2.274\times10^{-10}\text{m}\right)} = 611\times10^{3}\text{J mol}^{-1}$$

The dissociation energy

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

This is 10% over the experimental value of 489 kJ mol^{-1}, mainly because repulsions were neglected.

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

3.30 Repulsion between the lone pairs on the two F atoms causes an increase in bond length.

3.32 The polarity of the bonds follows the difference Δ in the electronegativities of the two atoms. These differences are given in parentheses in the following ranking

IF (1.32) > ClF (0.82) > ICl (0.50) > BrCl (0.20) > ClCl (0.0)

3.34 **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.

3.36

$$\delta = \frac{\left(0.2082 \quad \text{debys}^{-1}\right)}{R}\mu = \frac{0.2082 \quad \text{D}^{-1}}{0.980}\left(1.66\ \text{D}\right) = 0.353 \text{ for OH}\left(35.3\%\right)$$
$$\delta = \frac{\left(0.2082 \quad \text{D}^{-1}\right)}{1.131}\left(1.46\ \text{D}\right) = 0.269 \text{ for CH}\left(26.9\%\right)$$
$$\delta = \frac{0.2082 \quad \text{D}^{-1}}{1.175}\left(1.45\ \text{D}\right) = 0.257 \text{ for CN}\left(25.7\%\right)$$
$$\delta = 0 \text{ for } C_2$$

3.38 The third and fourth columns of the following table contain the comparison. Note that the absolute value of Δ must 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%

a) ClO_4^-: The formal charge on the central chlorine atom in this Lewis diagram is +3; all four oxygen atoms have formal charges −1.

b) SO_2: The formal charge of the sulfur in this Lewis diagram is +1; the left-hand oxygen has a formal charge of −1; the right-hand oxygen has a formal charge of 0.

c) BrO_2^-: The formal charge on the bromine in this representation is +1. The two oxygens both have formal charges of −1.

d) NO_3^-: The formal charge on the nitrogen in this Lewis diagram is +1. The left oxygen has a formal charge of 0, and the other two oxygen atoms have formal charges of −1.

3.42 In the Cl–Cl–O structure, the central Cl atom has formal charge +1, the O atom has f.c. −1, and the terminal CI has f.c. 0. In the Cl–O–Cl structure, each atom has f.c. 0. The second structure is favored because it shows less separation of formal charge.

3.44 **a)** The "Z" represents a Group V element. An example that actually exists is the CN^-(cyanide) ion.

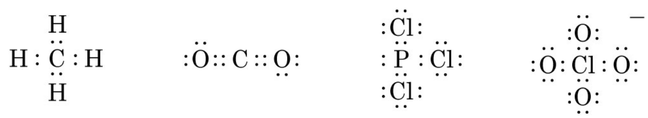
b) The unknown main-group element is a Group VII element. An example that actually exists is the ClO_4^- ion (perchlorate ion).

c) The unknown main-group element is a Group VI element. An example that actually exists is the SO_3^{2-} (sulfite) ion.

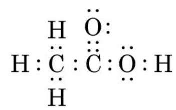
e) The "Z" is a Group V element. An example An example that actually exists is H_2NNH_2 (hydrazine).

3.46 The Lewis dot structures are

a) **b)** **c)** **d)**



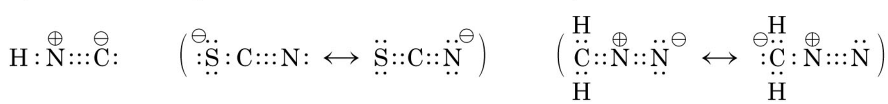
3.48 The best single Lewis structure is



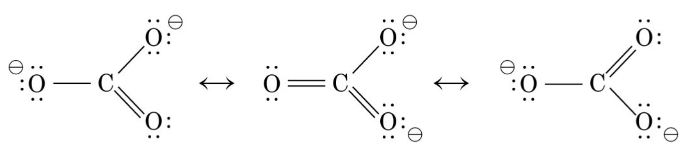
The C—H bond lengths are estimated to be 1.10 × 10^{-10} m, the C—C bond length is 1.54 × 10^{-10} m, the C=O bond length is 1.20 × 10^{-10} m, the C—O bond length is 1.43 × 10^{-10} m, and the O—H bond length is 0.96 × 10^{-10} m.

3.50 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.

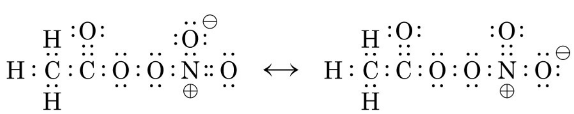
3.52 **a)** **b)** **c)**



3.54 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).

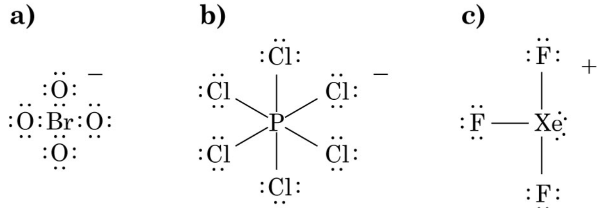


3.56



3.58 The valence octet is expanded in parts **b)** and **c)**, which should be XeF_3^+, not XeF_6^+.

a) **b)** **c)**



3.60 **a)** Phosphorus trifiuoride has a central P with *SN* 4. The molecule is trigonal pyramidal, like NH_3 (text Figure 3.17c).

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 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.

3.62 **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°.

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

3.66 **a)** Polar. **b)** Polar. **c)** Nonpolar. **d)** Polar. **e)** Nonpolar.

3.68 **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 3.20b) 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. The formulation $(SbCl_2^+)(GaCl_4^-)$is more likely correct.

3.70 **a)** The observation of a non-zero dipole moment for O_3 rules out a symmetrical straight-line geometry for the molecule. The molecule is either non-symmetrical linear (the three atoms in a straight line but unevenly spaced) or is bent.

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

3.72 $\overset{-3}{N}\overset{+1}{H_4}\overset{+5}{N}\overset{-2}{O_3}$ $\overset{+2}{Ca}\overset{+2}{Mg}\overset{+4}{Si}\overset{-2}{O_4}$ $\overset{+2}{Fe}(\overset{+2}{C}\overset{-3}{N})_6^{4-}$ $\overset{-3}{B_2}\overset{+1}{H_6}$

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

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

3.74 **a)** $GaBr_3$, gallium bromide $\cdot\dot{Ga}\cdot + 3\ :\ddot{\underset{..}{Br}}\cdot \rightarrow (Ga^{3+})\left(:\ddot{\underset{..}{Br}}:^-\right)_3$

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

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

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

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

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

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

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

3.84 **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

3.86 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 $\Delta\, EN$ in NaI. The compound between Cs and Au can reasonably be formulated as $Cs^+ \cdots Au^-$.

3.88 **a)** The ΔE (called ΔE_∞) of the first reaction is the first ionization energy IE_1 of Na(*g*) added to the negative of the *EA* (electron affinity) of I(*g*). Taking data from Appendix F gives

$$\Delta E_\infty = 495.8 + (-295.2) = 200.6 \text{ kJ mol}^{-1}$$

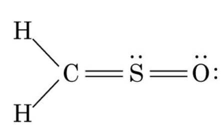
The ΔE_∞ of the second reaction is the *IE* of I(*g*) added to the negative of the electron affinity of Na(*g*). It is $\Delta E = 1008.4 + (-52.867) = 955.5 \text{ kJ mol}^{-1}$.

b) A similar combination of ionization energies and electron affinities of K and Cl gives ΔE_∞ of the first reaction as 69.8 kJ mol^{-1} and ΔE_∞ of the second reaction as 1202.7 kJ mol^{-1}.

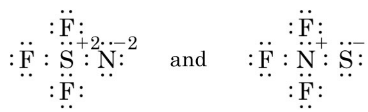
Even if $Na^-I^+(g)$ and $K^-\ Cl^+(g)$ were to form, the reactions transferring electrons to form $Na^+I^-(g)$ or $K^+Cl^-(g)$ would be strongly favored energetically and would occur quickly.

3.90 **a)** In the Lewis structure on the left, the H's and the C have f.c.'s of 0; the sulfur has f.c. +1, and the oxygen has f.c. −1. In the structure on the right, the H's and the O have f.c.'s 0; the carbon has f.c. −1, and the sulfur has f.c. +1.

b) The only way to draw a Lewis structure for sulfine in which all atoms have formal charges of zero is to violate the octet rule for the sulfur atom:

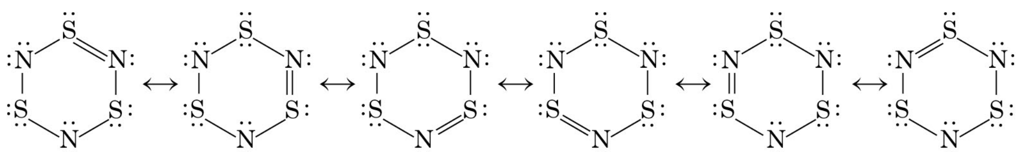


3.92 **a)** Lewis diagrams for the suggested isomers of SF_3N follow. The octet rule is satisfied on all the atoms in these structures.



b) Of the two structures, the one having a central N (shown on the right) is preferred. It has smaller formal charges. Additional resonance structures for both isomers are possible. Repositioning four electrons in the structure on the left from lone pairs on the N to shared pairs between the N and S leads to a 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.

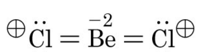
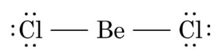
3.94 **a)**

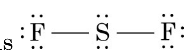


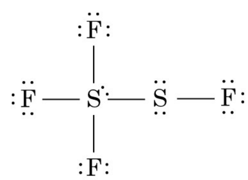
b) In every resonance structure, the S that is involved in the double bond has a formal charge of +1 while the two N's that are *not* involved in the double bond have formal charges of −1. The other N and S's have formal charges of zero.

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 ≈ −1.

3.96 **a)**  **b)** 

3.98 A Lewis structure for the monomer is  and the dimer is



Valence expansion is necessary for S_2F_4. The molecule has 40 valence electrons; 48 would be required to put separate octets on the 6 atoms. The known structure requires sharing at least 10 valence electrons. The difference 48 – 10 is less than the number of valence electrons that must be accommodated.

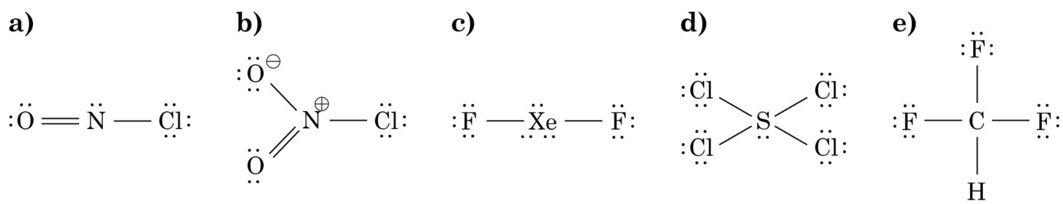
3.100 For KCl(g): $\mu = 10.3$ D; R = 2.67Å. If the KCl(g) molecule were completely ionic, its dipole moment would be

$$\mu = \frac{2.67\times10^{-10}\text{m}\times1.602\times10^{-19}\text{C}}{3.336\times10^{-30}\ \text{C m D}^{-1}} = 12.82\text{D}$$

As it is, the ionicity is less than total: $\delta = 10.3\ \text{D}/12.82\ \text{D} = 0.803\ (80.3\%)$.

3.102 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).

3.104 The Lewis dot structures are



The ONCl 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 seesaw geometry and is polar; the CHF_3 molecule is (nearly) tetrahedral and polar.

3.106 $2\overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} \rightarrow \overset{+1}{K_2}\overset{+6}{Mn}\overset{-2}{O_4} + \overset{+4}{Mn}\overset{-2}{O_2} + \overset{0}{O_2}$

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.

3.108 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.

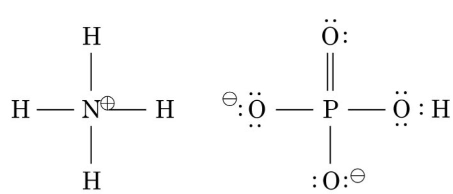
3.110 Element 114 is a group IV element that should have a maximum oxidation state of +4. However, the chemistry of heavier elements in this group (such as Pb) is dominated by the +2 oxidation state, so this should be true of element 114 as well.

3.112 Assume 100.00 g of compound, and use the procedure of text Section 2.3 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



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

b) Calculate the molecular masses by summing up the individual atomic masses of the elements in the compound each multiplied by the number of times it appears in the formula. 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

Introduction to Quantum Mechanics

4.2 The wavelength of this chemical wave is 1.2 cm; its frequency is 1/42 Hz (or s^{-1}). The speed of propagation is the product of these two quantities, 0.029 cm s^{-1}.

4.4 Substitute in the equation $c = \lambda\nu$. Assume that the gamma rays are propagating through a vacuum. The wavelength is then

$$\lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m s}^{-1}}{2.83\times10^{20}\text{s}^{-1}} = 1.06\times10^{-12}\,\text{m} = 0.0106\ \text{Å}$$

4.6 **a)** $\nu = c/\lambda = (2.9979\times10^{8}\ \text{m s}^{-1})\,/\,(488\times10^{-9}\ \text{m}) = 6.14\times10^{14}\text{s}^{-1}$.
b) Divide twice the distance between the Earth and Moon by the speed of light. The answer is 2.5 s.

4.8 The wavelength of the ultrasonic wave is its speed of propagation divided by its frequency. It comes out to 0.030 m, or 3.0 cm. The resolution in the sonic image is never better than the wavelength of sound used. If lower frequency ($\nu = 8000\ \text{s}^{-1}$) is used, then the wavelength is longer (18.7 cm), and the image of the fetus deteriorates to a blur.

4.10 It is instructive to compute the ratio instead of estimating it from Figure 4.8. Text equation 4.4 gives the necessary relationship: the radiant energy per unit volume in a blackbody as a function of temperature and frequency

$$\rho_T(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/\kappa_B T} - 1}$$

This quantity is an energy density per unit frequency (SI units: joule per cubic meter per hertz). Compute the two frequencies from the given wavelengths and the speed of light:

$$\nu_1 = 3\times10^{14}\text{s}^{-1}\ \text{(in the IR) and }\ \nu_2 = 6\times10^{14}\text{s}^{-1}\ \text{(in the visible)}$$

Write down the equation for each frequency and divide the first equation by the second

$$\frac{\rho_T(\nu_1)}{\rho_T(\nu_2)} = \left(\frac{\nu_1}{\nu_2}\right)^3 \frac{e^{h\nu_2/\kappa_B T} - 1}{e^{h\nu_1/\kappa_B T} - 1}$$

The ratio h/kB in the exponentials equals $4.80\times10^{-11}\,\text{K s}$. Substitute it into the equation along with the temperature and the two frequencies

$$\frac{\rho_{5000}(\nu_1)}{\rho_{5000}(\nu_2)} = \left(\frac{3.0\times10^{14}\,\text{s}^{-1}}{6.0\times10^{14}\,\text{s}^{-1}}\right)^3 \left(\frac{e^{(4.80\times10^{-11}\,\text{K s})(6.0\times10^{14}\,\text{s}^{-1})/(5\,000\ \text{K})}-1}{e^{(4.80\times10^{-11}\,\text{K s})(3.0\times10^{14}\,\text{s}^{-1})/(5\,000\ \text{K})}-1}\right)$$

$$= \frac{1}{8}\left(\frac{e^{5.76}-1}{e^{2.88}-1}\right) = \frac{1}{8}\left(\frac{317.35-1}{17.81-1}\right) = 2.35$$

Repeat with a higher temperature. Using 10 000 K makes the re-computation easy

$$\frac{\rho_{10000}(\nu_1)}{\rho_{10000}(\nu_2)} = \frac{1}{8}\left(\frac{e^{2.88}-1}{e^{1.44}-1}\right) = \frac{1}{8}\left(\frac{17.18-1}{4.22-1}\right) = 0.652$$

The ratio decreases with increasing temperature. Both exponentials decrease, but the one in the numerator decreases faster. The change corresponds to a shift in intensity toward the blue (higher frequency, shorter wavelength) as T increases.

4.12 A wavelength of 454 nm is in the blue region of the spectrum.

4.14 The energy lost by the potassium atom is carried away by a single photon. The wavelength of the photon is

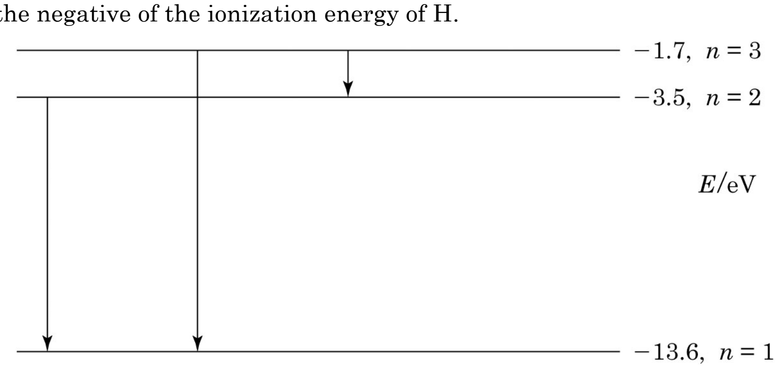
$$\lambda = \frac{hc}{E} = \frac{(6.626\times10^{-34}\,\text{J s})(2.9979\times10^{8}\,\text{m s}^{-1})}{4.9\times10^{-19}\,\text{J}} = 4.1\times10^{-7}\,\text{m} = 410\ \text{nm}$$

This wavelength is in the violet region of the spectrum.

4.16 **a)** The energy transmitted by a photon is $E = h\nu = hc/\lambda$. In this case $E = 3.8\times10^{-19}$ J.
b) The power of the laser is 10 W, which is10 J s^{-1}. Hence

$$\text{rate of emission} = 10\ \text{J s}^{-1}\times\left(\frac{1\ \text{photon}}{3.82\times10^{-19}\,\text{J}}\right) = 2.6\times10^{19}\,\text{photons s}^{-1}$$

4.18 The 10.1 eV threshold in the Franck-Hertz experiment on H corresponds to the $n = 1 \rightarrow n = 2$ transition; the 11.9 eV threshold corresponds to the $n = 1 \rightarrow n = 3$ transition. Transitions in the emission spectrum connect these levels pair-wise, as indicated by the descending arrows in the following diagram. The diagram follows convention by setting the energy of the $n = 1$ state at –13.6 eV, the negative of the ionization energy of H.



Text Example 4.2 gives an equation for the wavelength of the photons emitted in spectroscopic transitions in terms of the Franck-Hertz threshold voltage

$$\lambda = \frac{1}{V_{\text{thr}}}(1239.8 \text{ nm V})$$

where V_{thr} is the threshold voltage. Substituting V_{thr} = 10.1, 11.9, and 1.8 V (the last of these comes from the energy difference between the n = 2 and n = 3 states) gives wavelengths of 123 nm, 104 nm, and 6.9×10^{2} nm, respectively. These results are in acceptable agreement with 121.5 nm, 102.5 nm, and 656.1 nm, which are the wavelengths for the three transitions as calculated using Bohr theory (see text equation 4.16). A threshold voltage of 1.8 V is not directly observed in the Franck-Hertz experiment because very few H atoms are in the n = 2 state at ordinary temperatures.

4.20 According to the Bohr model, the radius of a one-electron atom or ion is

$$r_n = \frac{n^2}{Z}a_o = \frac{n^2}{Z}(5.29\times10^{-11} \text{ m})$$

Substitution of Z = 2 (for helium) and n = 5 gives $r = 6.61\times10^{-10}$ m. The energy of an allowed state of a one-electron atom or ion is

$$E_n = -\frac{Z^2}{n^2}(2.18\times10^{-18} \text{ J})$$

For He^{+} ion in the n = 5 state, this energy equals -3.49×10^{-19} J. Removing the electron means changing the energy of the ion to E = 0. The change in energy is this final value minus the initial value, or $+3.49\times10^{-19}$. For a mole of atoms the energy change is Avogadro's number times larger or 210 kJ mol^{-1}. The energy of a He^{+} ion in the n = 3 state is -9.69×10^{-19} J. The change in energy of a He^{+} ion in the 5 $\rightarrow$ 3 transition equals

$$\Delta E = E_3 - E_5 = -9.69\times10^{-19} \text{ J} - \left(-3.49\times10^{-19} \text{ J}\right) = -6.20\times10^{-19} \text{ J}$$

The transition gives off energy, as shown by the negative ΔE. The frequency of the photon that carries away this energy is $9.36\times10^{14}\text{s}^{-1}$, and the wavelength is 320 nm.

4.22 In the spectrum of Be^{3+} (in which Z = 4) the series of lines analogous to the Lyman series of atomic hydrogen has wavelengths equal to 1/16 of the wavelengths of the Lyman series; the frequencies in this series are 16 times the frequencies in the Lyman series. A similar scaling occurs with the series analogous to the Balmer series. These conclusions follow from the dependence of the energy of the states of hydrogen-like ions on Z^2. Thus, for the frequencies in the Lyman-like series

$$\nu = (16)\times3.29\times10^{15}\left(\frac{1}{1^2} - \frac{1}{n_{\text{final}}^2}\right)\text{s}^{-1}$$

The n's for the first three n_{final}'s are 3.95 × 10^{16}, 4.68 × 10^{16}, and 4.94 × 10^{16} s^{-1}. The corresponding wavelengths are 7.59, 6.41, and 6.07 nm, in the x-ray region.
For the frequencies in the Balmer-like series

$$\nu = (16)\times3.29\times10^{15}\left(\frac{1}{2^2} - \frac{1}{n_{\text{final}}^2}\right)\text{s}^{-1}$$

The n's for the first three n_{final}'s are 7.31 × 10^{15}, 9.87 × 10^{15}, and 1.11 × 10^{16} s^{-1}. The corresponding wavelengths are 41.0, 30.4, and 27.1 nm, in the ultraviolet region.

4.24 The red light has lower frequency and hence lower energy than the green light. If green light ejects no electrons from the copper surface, then red light also ejects no electrons.

4.26 The maximum-wavelength light supplies photons that are just energetic enough to overcome the work function of the sodium surface

$$\lambda_{\text{max}} = \frac{hc}{E} = \frac{hc}{\Phi_{\text{Na}}} = \frac{\left(6.626\times10^{-34}\,\text{J s}\right)\left(2.998\times10^{8}\,\text{m s}^{-1}\right)}{4.41\times10^{-19}\,\text{J}} = 4.50\times10^{-7}\,\text{m}$$

4.28 A maximum-wavelength photon supplies just enough energy to overcome the work function of the tungsten surface

$$\lambda_{\text{max}} = \frac{hc}{\Phi_{\text{W}}} = \frac{\left(6.626\times10^{-34}\ \text{J s}\right)\left(2.9979\times10^{8}\text{m s}^{-1}\right)}{7.29\times10^{-19}\,\text{J}} = 272\times10^{-9}\text{m} = 272\ \text{nm}$$

The ejected electrons are to have a maximum velocity of 2.00×10^6 m s^{-1}. The maximum kinetic energy of such electrons is

$$\mathcal{T}_{\text{max}} = \tfrac{1}{2}mv^2 = \tfrac{1}{2}\left(9.109\times10^{-31}\ \text{kg}\right)\left(2.00\times10^{6}\ \text{m s}^{-1}\right)^2 = 1.82\times10^{-18}\ \text{J}$$

The wavelength of the required photon is

$$\lambda = \frac{hc}{\Phi_{\text{W}} + \mathcal{T}_{\text{max}}} = \frac{\left(6.626\times10^{-34}\text{J s}\right)\left(2.9979\times10^{8}\text{m s}^{-1}\right)}{\left(7.29\times10^{-19} + 1.82\times10^{-18}\right)\ \text{J}} = 77.9\times10^{-9}\text{m} = 77.9\ \text{mn}$$

4.30 **a)** In the ground state, one half-wavelength fits along the length of the bond, which is 1.0 Å. Hence $l_1 = 2.0$ Å. In the first excited state (n = 2), two half-wavelengths fit: $l_2 = 1.0$ Å.
b) The number of nodes is one less than the quantum number describing the standing wave. Hence, there is 1 node in the wave-function of the n = 2 state (the first excited state).

4.32 **a)** Compute the momentum of the electrons and substitute the result in the DeBroglie formula

$$p_{\text{e}} = m_{\text{e}}v = \sqrt{m_{\text{e}}^2 v^2} = \sqrt{2m_{\text{e}}\mathcal{T}}$$

$$\lambda = \frac{h}{p_{\text{e}}} = \frac{h}{\sqrt{2m_{\text{e}}\mathcal{T}}} = \frac{6.626\times10^{-34}\text{J s}}{\sqrt{2\left(9.109\times10^{-31}\text{kg}\right)\left(1.20\times10^{7}\text{J mol}^{-1}/6.022\times10^{23}\text{mol}^{-1}\right)}}$$

$$= 0.110\times10^{-9}\ \text{m}$$

where the kinetic energy $\mathcal{T}$ has been put on a per-particle basis by dividing it by Avogadro's number.
b) A helium atom moving at 353 m s^{-1} has a wavelength of

$$\lambda_{\text{He}} = \frac{h}{p} = \frac{h}{mv} = \frac{6.626\times10^{-34}\text{J s}}{\left(4.0026\ \text{u}/6.022\times10^{26}\text{u kg}^{-1}\right)\left(353\ \text{m s}^{-1}\right)} = 0.282\times10^{-9}\ \text{m}$$

c) A krypton atom moving at 299 m s^{-1} has a wavelength of

$$\lambda_{\text{Kr}} = \frac{h}{p} = \frac{h}{mv} = \frac{6.626\times10^{-34}\text{J s}}{\left(83.798\ \text{u}/6.022\times10^{26}\text{u kg}^{-1}\right)(299\ \text{m s}^{-1})} = 0.0159\times10^{-9}\ \text{m}$$

4.34 The problem concerns low-energy electron diffraction (see problem **4.33**). In the LEED experiment the possible angles of diffraction are given by the equation

$$D\sin\phi = n\lambda_e \quad \text{which leads to} \quad \lambda_e = \frac{\sin\phi}{n}D$$

where ϕ is the angle between the incoming beam of electrons, which is normal to the surface, and the diffracted beam. This differs from Bragg's law (text equation 4.24) by a factor of 2. The problem asks for the energy required to obtain the diffraction pattern. Take this to mean the minimum energy required for any diffraction to occur. Minimum energy goes with maximum wavelength for particles. The maximum λ_e in the governing equation occurs at the maximum sin ϕ, which is 1, and at minimum n, which also is 1. The maximum λ_e for diffraction in this experiment is therefore 4.0 Å. The kinetic energy of 4.0 Å electrons is

$$\mathcal{T} = \frac{h^2}{2m_e\lambda^2} = \frac{(6.626\times10^{-34}\ \text{J s})^2}{2(9.11\times10^{-31}\ \text{kg})(4.0\times10^{-10}\ \text{m})^2} = 1.507\times10^{-18}\ \text{J} = 9.41\ \text{eV}$$

The diffraction of 9.41 eV electrons occurs at f = 90°, which corresponds to the diffracted beam shooting out parallel to the surface. The energy of the electrons would have to exceed 9.41 eV before a useful diffraction pattern could be observed.

4.36 **a)** Use the Heisenberg indeterminacy principle

$$\Delta x \cdot \Delta(mv) \geq h/4\pi$$

with m = 9.109 × 10^{-31} kg and v = 3.0 × 10^{8} m s^{-1}. The result is $\Delta x \geq 1.93\times10^{-13}$m. This is 0.002 Å.

b) Because the helium atom is much more massive its Δx is much smaller. Repeat the computation with $m = m_{He}$ = 6.646 × 10^{-27} kg. The result is 2.65 × 10^{-17} m.

4.38 Compute the ΔE of the solvated electrons in their "box" as they transition from their ground state to the first excited state

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ \text{J s})(2.9979\times10^{8}\ \text{m s}^{-1})}{800\times10^{-9}\ \text{m}} = 2.483\times10^{-19}\ \text{J}$$

The energies of the two levels, which have quantum numbers (2,1,1) and (1,1,1) are given by text equation 4.40 (by assumption). Compute the difference between the two energies and set it equal to the preceding ΔE

$$\Delta E = \frac{h^2}{8m_eL^2}\left[(2^2+1^2+1^2)-(1^2+1^2+1^2)\right]$$

$$2.483\times10^{-19}\ \text{J} = \frac{h^2}{8m_eL^2}[3]$$

$$L = \sqrt{\frac{(6.626\times10^{-34}\ \text{J s})^2[3]}{8(9.109\times10^{-31}\ \text{kg})(2.483\times10^{-19}\ \text{J})}} = 8.53\times10^{-10}\ \text{m} = 8.53$$

4.40 **a)** The wave-function for the (100,100) excited state for a particle in a square box of side L is

$$\psi_{100,100} = \sqrt{\frac{4}{L^2}}\sin\frac{(100)\pi x}{L}\sin\frac{(100)\pi y}{L}$$

This wave-function has a total of 198 straight-line nodes (99 perpendicular to the x axis and 99 perpendicular to the y axis). It has 10 000 local probability maxima.

b) The particle, which is in a high-energy state, is moving rapidly (is highly delocalized). The probability of finding it in the close vicinity of point (x, y) is proportional to the square of y

$$\psi^2_{100,000} = \frac{4}{L^2}\sin^2\frac{(100)\pi\ x}{L}\sin^2\frac{(100)\pi\ y}{L}$$

The particle clearly has an equal probability of existing within each of the 10 000 small squares defined by the nodes (and the walls of the box). Its probability of being within any one of the small squares at a given instant is 0.0001; its most likely location within a given small square is at the center of the square. The probability of being at (on) any of the nodes is 0 yet the particle passes from one small square to the next with ease.

4.42 The wave-function is

$$\psi_{222} = \sqrt{\frac{8}{L^3}}\sin\frac{2\pi x}{L}\sin\frac{2\pi y}{L}\sin\frac{2\pi z}{L}$$

a) This wave-function depends on x according to $\sin 2\pi x / L$. If x equals 0.50 L, $c_{222} = 0$ because $\sin 2\pi(0.50L)/L = \sin 180° = 0$. The $x = 0.5L$ plane is a node.

b) By similar reasoning the $y = 0.5L$ plane is also a node (as is the $z = 0.5L$ plane).

4.44 The time it takes for any electromagnetic waves to arrive from Cygnus A is its distance divided by the speed of light. This is 3×10^{24} m divided by 3.00×10^{8} m s^{-1} or 10^{16} s, which equals 3×10^{8} years. In other words, Cygnus A is 300 million light-years away. The frequency of the radio wave is c divided by its wave-length. It is 3.0×10^{7} s^{-1}.

4.46

$$E_{\text{x-ray}} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\text{ J s}\times3.00\times10^{8}\text{ m s}^{-1}}{0.20\times10^{-9}\text{ m}} = 9.9\times10^{-16}\text{ J}$$

$$E_{\text{AM radio}} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\text{ J s}\times3.00\times10^{8}\text{ m s}^{-1}}{200\text{ m}} = 9.9\times10^{-28}\text{ J}$$

The x-ray photon is capable of inducing a chemical reaction for which the required energy is 6.0×10^{5} kJ mol^{-1}. (This greatly exceeds the dissociation energy of every chemical bond). The AM radio photon has an energy of only 6.0×10^{-4} J mol^{-1} and is ineffective in influencing chemical reactions.

4.48 **a)** The energy barrier is the work function F_{Cd}

$$\Phi_{Cd} = E_{\text{photon,min}} = \frac{hc}{\lambda_{\text{max}}} = \frac{(6.626\times10^{-34}\text{ J s})(2.998\times10^{8}\text{ m s}^{-1})}{315\times10^{-9}\text{m}}$$
$$= 6.31\times10^{-19}\text{ J} = 3.94\text{ eV} = 380\text{ kJ mol}^{-1}$$

b)

$$E_{\text{photon}} = \mathcal{T}_{\text{max}} + \Phi_{\text{Cd}}$$

$$\begin{aligned}\mathcal{T}_{\text{max}} &= E_{\text{photon}} - \Phi_{\text{Cd}} = \frac{hc}{\lambda} - 6.306\times10^{-19}\,\text{J}\\ &= \frac{(6.626\times10^{-34}\ \text{J s})(2.998\times10^{8}\ \text{m s}^{-1})}{200\times10^{-9}\ \text{m}} - 6.306\times10^{-19}\ \text{J}\\ &= 9.932\times10^{-19} - 6.306\times10^{-19}\ \text{J}\\ &= 3.63\times10^{-19}\ \text{J} = 2.26\ \text{eV} = 218\ \text{kJ mol}^{-1}\end{aligned}$$

c) Compute the momentum of the 2.26 eV electrons and then the corresponding wavelength

$$\begin{aligned}p_{\text{e}} &= m_{\text{e}}\upsilon = \sqrt{m_{\text{e}}^2\upsilon_{\text{max}}^2} = \sqrt{2m_{\text{e}}\mathcal{T}}\\ &= \sqrt{2(9.109\times10^{-31}\,\text{kg})(3.626\times10^{-19}\,\text{kg m}^2\text{s}^{-2})} = 8.13\times10^{-25}\ \text{kg m s}^{-1}\end{aligned}$$

$$\lambda = \frac{h}{p_{\text{e}}} = \frac{6.626\times10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{8.128\times10^{-25}\ \text{kg m s}^{-1}} = 8.15\times10^{-10}\ \text{m} = 0.815\ \text{nm}$$

4.50 Obtain a formula for the quantized speed of an electron in its orbit in a hydrogen-like ion by eliminating r between

$$\upsilon = \frac{n\ h}{2\pi m_{\text{e}} r} \quad \text{and} \quad r = \frac{\epsilon_0 n^2 h^2}{\pi Z e^2 m_{\text{e}}}$$

The result is

$$\upsilon = \frac{n\ h}{2\pi m_{\text{e}}}\frac{\pi Z e^2 m_{\text{e}}}{\epsilon_0 n^2 h^2} = \left(\frac{Z}{n}\right)\frac{e^2}{2\epsilon_0 h}$$

Substitute appropriate values from the problem

$$\upsilon_{\text{e}}(\text{in He}^+) = \left(\frac{2}{1}\right)\frac{(1.60218\times10^{-19}\ \text{C})^2}{2(8.8542\times10^{-12}\ \text{C}^2\ \text{J}^{-1}\text{m}^{-1})(6.626\times10^{-34}\ \text{J s})} = 4.375\times10^{6}\text{m s}^{-1}$$

$$\upsilon_{\text{e}}(\text{in U}^{91+}) = \left(\frac{92}{1}\right)\frac{(1.60218\times10^{-19}\,\text{C})^2}{2(8.8542\times10^{-12}\,\text{C}^2\ \text{J}^{-1}\text{m}^{-1})(6.626\times10^{-34}\ \text{J s})} = 2.013\times10^{8}\ \text{m s}^{-1}$$

The speed of light is 3.00×10^8 m s^{-1}. Relativistic effects will be important in U^{91+}, but negligible in He^+.

4.52 The C^{5+} ion is a hydrogen-like ion with $Z = 6$. All transitions in its spectrum have frequencies that fit the following formula with $Z = 6$ and whole-number n:

$$\nu = \frac{c}{\lambda} = -Z^2(3.29\times10^{15}\text{s}^{-1})\left(\frac{1}{n_{\text{initial}}^2} - \frac{1}{n_{\text{final}}^2}\right)$$

Take green light to have wavelengths ranging from 500 to 550 nm (text Figure 4.3). Insert these wavelengths expressed in meters, $Z = 6$, and c in m s^{-1} into the formula. The units cancel out and

$$\left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right) = 0.00460 \text{ to } 0.00506$$

Now, systematically try combinations of integers until a combination that gives the desired result is found. Note that n_{final} must be less than n_{initial}. The first combination that works is $n_{\text{initial}} = 8$ and $n_{\text{final}} = 7$ for which

$$\left(\frac{1}{7^2} - \frac{1}{8^2}\right) = 0.00478$$

4.54 **a)** Destructive interference supersedes constructive interference as the distance between the two loudspeakers changes. Destructive interference occurs when one wave-train lags the other by 1, 2, 3 ... half-wavelengths. The half-wavelength $1/2\lambda$ is thus 0.16 (or 0.080 or 0.0533...) m, and λ is 0.32 m. Take 0.32 m as the answer because minima in the intensity of the tone would have been noticed at movement distances equal to less than 0.16 m if the wavelength were shorter.
b) The frequency is the speed of the sound divided by its wavelength. It is $1.1 \times 10^3\ \text{s}^{-1}$.

4.56

$$\Delta E = \frac{h}{4\pi\Delta t} = \frac{6.626 \times 10^{-34}\ \text{J s}}{4\pi\left(10^{-10}\ \text{s}\right)} = 5.3 \times 10^{-25}\,\text{J} \quad \Delta\nu = \frac{\Delta E}{h} = \frac{1}{4\pi\Delta t} = 8.0 \times 10^{8}\ \text{s}^{-1}$$

4.58 **a)** In the different universe ordinary objects in motion at moderate speeds, such as baseballs, have substantial wavelengths

$$\lambda_{\text{baseball}} = \frac{h}{mv} = \frac{1\ \text{J s}}{0.145\ \text{kg} \times 20\ \text{m s}^{-1}} = 0.34\ \text{m}$$

b) Take the uncertainty in the velocity of the baseball Δv to be $2\,\text{m s}^{-1}$. Then

$$\Delta p_{\text{baseball}} = \left(0.145\ \text{kg}\right)\left(2\ \text{m s}^{-1}\right) = 0.29\ \text{kg m s}^{-1}$$

$$\Delta p_{\text{baseball}} \Delta x_{\text{baseball}} \geq \frac{h}{4\pi} = \frac{1\ \text{J s}}{4\pi} \quad \text{hence} \quad \Delta x_{\text{baseball}} \geq \frac{1\ \text{J s}}{4\pi\left(0.29\ \text{kg m s}^{-1}\right)} = 0.27\ \text{m}$$

This would make the baseball hard to catch.

c) The Bohr radius in the different universe is larger

$$a_0 = \frac{\epsilon_0 h^2}{\pi e^2 m_e} = \frac{\left(8.854 \times 10^{-12}\ \text{C}^2\ \text{J}^{-1}\ \text{m}^{-1}\right)\left(1\ \text{J s}\right)^2}{\pi\left(1\ \text{C}\right)^2\left(0.001\ \text{kg}\right)} = 2.82 \times 10^{-9}\ \text{m} = 28$$

4.60

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{(2L)^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}\right]$$

$$E_{111} = \frac{h^2}{8\ mL^2}(1/4+1+1) = \frac{9}{4}\frac{h^2}{8mL^2} \qquad E_{211} = \frac{h^2}{8\ mL^2}(4/4+1+1) = \frac{12}{4}\frac{h^2}{8mL^2}$$

$$E_{311} = \frac{h^2}{8\ mL^2}(9/4+1+1) = \frac{17}{4}\frac{h^2}{8mL^2} \qquad E_{112} = E_{121} = \frac{h^2}{8\ mL^2}(1/4+4+1) = \frac{21}{4}\frac{h^2}{8mL^2}$$

$$E_{411} = E_{221} = E_{212} = \frac{h^2}{8\ mL^2}(6) = \frac{24}{4}\frac{h^2}{8mL^2} \qquad E_{321} = E_{312} = \frac{h^2}{8\ mL^2}(9/4+4+1) = \frac{29}{4}\frac{h^2}{8mL^2}$$

The (111) state is the ground state; the others are excited states. Note the double degeneracy of two of the excited states and the triple degeneracy of a third.

Chapter 5

Quantum Mechanics and Atomic Structure

5.2 **a)** This combination is not allowed because m_s is never equal to zero. If m_s were changed to $\pm\frac{1}{2}$, this combination would be allowed.

b) This combination is allowed. It specifies a $2s$ electron.
c) This combination is allowed. It specifies a $7d$ electron.
d) This combination is not allowed. The quantum number ℓ is never negative.

5.4 **a)** $3d$ **b)** $7g$ **c)** $5p$.

5.6 **a)** A $3d$ orbital has 0 radial nodes and 2 angular nodes.
b) A $7g$-orbital has 2 radial and 4 angular nodes.
c) A $5p$-orbital has 3 radial and 1 angular node.

5.8 **a)**

$$R(3p) = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6\sigma - \sigma^2\right)\ \exp\left(-\frac{\sigma}{3}\right)$$

A node occurs when $R(3p) = 0$. The function equals zero when $6\sigma - \sigma^2 = 0$ which means it equals zero when $\sigma = 6$. The node is at $r = 6 \cdot a_0 = 6(0.529) = 3.17$.

b)

$$R(3s) = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\sigma + 2\sigma^2\right)\ \exp\left(-\frac{\sigma}{3}\right)$$

Nodes occur at the roots of $27 - 18\sigma + 2\sigma^2 = 0$

$$\frac{r}{a_0} = \sigma = \frac{18 \pm \sqrt{324 - 8\times 27}}{4} = 1.902,\ 7.098$$

$$r_1 = 1.902(0.529\quad) = 1.01 \qquad r_2 = 7.098(0.529\quad) = 3.75$$

5.10 Use text equation 5.7, which gives the average distance of the electron in hydrogen-like species

$$\bar{r}_{nl} = \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right\}$$

When the electron in He^+ ion is a 2*s* electron, $Z = 2$, $n = 2$, and $\ell = 0$

$$\bar{r}_{2,0} = \frac{2^2 a_0}{2}\left\{1 + \frac{1}{2}\left[1 - \frac{0(0+1)}{2^2}\right]\right\} = 3a_0 = 3(0.529\ \text{Å}) = 1.59\ \text{Å}$$

When the electron in He^+ ion is a 2*p* electron, $Z = 2$, $n = 2$, and $l = 1$

$$\bar{r}_{2,1} = \frac{2^2 a_0}{2}\left\{1 + \frac{1}{2}\left[1 - \frac{1(1+1)}{2^2}\right]\right\} = \frac{5}{2}a_0 = 1.32\ \text{Å}$$

The average distance of the 2*s* and 2*p* electrons (and electrons in all other states as well) in one-electron species depends on the reciprocal of *Z*. It therefore shrinks by 50% when the nuclear charge is doubled moving from H to He^+.

5.12 The problem gives $Z_{\text{eff}} = 1.02$ for a 2*p* ($n = 2$, $\ell = 1$) electron in Li. Substitute in text equations 5.9 and 5.10

$$\epsilon_{2p}(\text{Li}) \approx -\frac{\left[Z_{\text{eff}}(n)\right]^2}{n^2}\ \text{Ry} = -\frac{\left[1.02\right]^2}{2^2}\ \text{Ry} = -0.260\ \text{Ry} = -5.67\times10^{-19}\ \text{J} = -3.54\ \text{eV}$$

$$\bar{r}_{2p}(\text{Li}) \approx \frac{2^2 a_0}{1.02}\left\{1 + \frac{1}{2}\left[1 - \frac{1(1+1)}{2^2}\right]\right\} = \frac{2^2 a_0}{1.02}\left\{\frac{5}{4}\right\} = 4.90\ a_0 = 2.59$$

A 2*s* electron in Li (the subject of problem **5.11**) has about the same average distance from the nucleus as a 2*p* electron (2.52 Å versus 2.59 Å), but considerably lower energy (–5.40 eV versus –3.54 eV). This occurs because the 2*s* electron is very differently distributed. Its orbital penetrates to the nucleus while the 2*p* orbital has a node at the nucleus. Averages tell nothing about distribution. Good examples from everyday life are the distribution of personal income and the sale prices of houses.

5.14 Problem **5.13** gives $Z_{\text{eff}}(3s) = 1.84$ for the Na atom. Substitute this value into text equation 5.10 along with $n = 3$, $\ell = 0$

$$\bar{r}_{3s}(\text{Na}) \approx \frac{3^2 a_0}{1.84}\left\{1 + \frac{1}{2}\left[1 - \frac{0(0+1)}{3^2}\right]\right\} = \frac{3^2 a_0}{1.84}\left\{\frac{3}{2}\right\} = 7.33 a_0 = 3.88$$

Problem **5.11** gives $Z_{\text{eff}}(2s) = 1.26$ for the Li atom. Substitute this value and $n = 2$, $\ell = 0$ as in the previous

$$\bar{r}_{2s}(\text{Li}) \approx \frac{2^2 a_0}{1.26}\left\{1 + \frac{1}{2}\left[1 - \frac{0(0+1)}{2^2}\right]\right\} = \frac{2^2 a_0}{1.26}\left\{\frac{3}{2}\right\} = 4.76\ a_0 = 2.52\ \text{Å}$$

The effective nuclear charge in the H atom equals 1, the actual nuclear charge. Substitute this value and $n = 1$, $\ell = 0$

$$\bar{r}_{1s}(\text{H}) = \frac{1^2 a_0}{1}\left\{1+\frac{1}{2}\left[1-\frac{0(0+1)}{1^2}\right]\right\} = \frac{1^2 a_0}{1}\left\{\frac{3}{2}\right\} = 1.50\ a_0 = 0.794$$

The decrease in $\bar{r}$ moving from Na to Li to H indicates the decrease in the average distance of the valence electron in these species. It is not as sharp as the decrease in n^2 because of shielding by other electrons.

5.16 **a)** P: $[\text{Ne}]3s^2 3p^3$ **b)** Tc: $[\text{Kr}]4d^5 5s^2$ **c)** Ho: $[\text{Xe}]4f^{11} 6s^2$

5.18

Species	Ground-State Configuration	Magnetism
Li^-	$1s^2 2s^2$	diamagnetic
B^+	$1s^2 2s^2$	diamagnetic
F^-	$1s^2 2s^2 2p^6$	diamagnetic
Al^{3+}	$1s^2 2s^2 2p^6$	diamagnetic
S^-	$1s^2 2s^2 2p^6 3s^2 3p^5$	paramagnetic
Ar^+	$1s^2 2s^2 2p^6 3s^2 3p^5$	paramagnetic
Br^+	$[\text{Ar}]3d^{10} 4s^2 4p^4$	paramagnetic
Te^-	$[\text{Kr}]4d^{10} 5s^2 5p^5$	paramagnetic

A species having an odd number of electrons *must* be paramagnetic; a species having an even number of electrons *may* be paramagnetic or diamagnetic.

5.20 **a)** The species is an atom and is therefore electrically neutral. It has 76 electrons. The element with $Z = 76$ is osmium. **b)** The ion is F^-. **c)** The ion is Ag^{5+}.

5.22 **a)** This element would lie in Group I of the 8th row in the periodic table; it would have $Z = 119$.

b) The atomic number 137 exceeds 119 by 18. This difference could be explained by the filling of nine 5*g* orbitals by 18 electrons before the end of the 7th row of the periodic table. The 7th row would in this scenario contain a total of 50 elements.

5.24 The three noble-gas atoms would have $Z = 3$ (which corresponds to "$1s^3$"), $Z = 15(\text{"}1s^3 2s^3 2p^9\text{"})$, and $Z = 27(\text{"}1s^3 2s^3 2p^9 3s^3 3p^9\text{"})$.

5.26 **a)** The minimum energy to remove the electron from a ground-state H atom is 1 rydberg, which is 2.179×10^{-18} J. The wavelength of a photon supplying this much energy is

$$\lambda = \frac{hc}{E} = \frac{(6.626\times10^{-34}\ \text{J s})(2.9979\times10^{8}\ \text{m s}^{-1})}{2.179\times10^{-18}\ \text{J}} = 9.12\times10^{-8}\ \text{m} = 91.2\ \text{nm}$$

This is the *maximum* wavelength of radiation that can ionize a hydrogen atom. Radiation of wavelengths shorter than this also can ionize H atoms.
b) Solve the equation $\frac{1}{2}mv^2 = \Delta E$ for v and substitute

$$v = \sqrt{\frac{2\Delta E}{m}} = \sqrt{\frac{2(2.179\times10^{-18}\ \text{J})}{9.109\times10^{-31}\ \text{kg}}} = 2.19\times10^{6}\ \text{m s}^{-1}$$

Converting to miles per hour gives

$$v = 2.19\times10^{6}\ \text{m s}^{-1}\left(\frac{1\ \text{ft}}{0.3048\ \text{m}}\right)\left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right) = 4.89\times10^{6}\ \text{mi h}^{-1}$$

c) For thermal excitation, $k_B T \approx \Delta E$

$$T \approx \frac{\Delta E}{k_B} = \frac{2.179\times10^{-18}\ \text{J}}{1.381\times10^{-23}\ \text{J K}^{-1}} = 1.58\times10^{5}\ \text{K}$$

5.28 In some printings of the textbook the speeds of the electrons in the four peaks are not correct. The correct values are

Peak	Speed of Electrons	Peak	Speed of Electrons
1	2.097×10^{7} m s^{-1}	3	2.014×10^{7} m s^{-1}
2	2.093×10^{7}	4	1.971×10^{7}

a) The energy of the x-radiation used to irradiate the silicon atoms in this experiment is

$$E_{\text{x-rays}} = h\nu = \frac{hc}{\lambda} = \frac{(6.62607\times10^{-34}\ \text{J s})(2.99792\times10^{8}\ \text{m s}^{-1})}{9.890\times10^{-10}\ \text{m}} = 2.0085\times10^{-16}\ \text{J}$$
$$= 2.0085\times10^{-16}\text{J}\left(\frac{1\ \text{eV}}{1.6022\times10^{-19}\ \text{J}}\right) = 1253.6\ \text{eV}$$

Use the equation

$$IE = h\nu - \tfrac{1}{2}m_e v^2$$

as follows

$$IE_1 = 1253.6\ \text{eV} - \frac{(9.10938\times10^{-31}\ \text{kg})(2.097\times10^{7}\ \text{m s}^{-1})^2}{2}\left(\frac{1\ \text{eV}}{1.6022\times10^{-19}\ \text{J}}\right) = 3.5\ \text{eV}$$

$$IE_2 = 1253.6\ \text{eV} - \frac{(9.10938\times10^{-31}\ \text{kg})(2.093\times10^{7}\ \text{m s}^{-1})^2}{2}\left(\frac{1\ \text{eV}}{1.6022\times10^{-19}\ \text{J}}\right) = 8.3\ \text{eV}$$

$$IE_3 = 1253.6\ \text{eV} - \frac{(9.10938\times10^{-31}\ \text{kg})(2.014\times10^{7}\ \text{m s}^{-1})^2}{2}\left(\frac{1\ \text{eV}}{1.6022\times10^{-19}\ \text{J}}\right) = 100.5\ \text{eV}$$

$$IE_4 = 1253.6\ \text{eV} - \frac{(9.10938\times10^{-31}\ \text{kg})(1.971\times10^{7}\ \text{m s}^{-1})^2}{2}\left(\frac{1\ \text{eV}}{1.6022\times10^{-19}\ \text{J}}\right) = 149.2\ \text{eV}$$

b) The ground-state electron configuration of silicon is $1s^2 2s^2 2p^6 3s^2 3p^2$. Peak 1 corresponds to removal of silicon's $3p$ electrons, which are its least tightly bound electrons. Peaks 2, 3, and 4 correspond to removal of Si's $3s$, $2p$, and $2s$ electrons respectively. The $1s$ electron does not give a peak. It is probably at an energy lower than –1253.6 eV and inaccessible with the x-radiation used in this experiment.

5.30 From text equation 5.9

$$Z_{\text{eff}}(n) \approx \sqrt{n^2\left(-\epsilon_n\left(\text{in rydbergs}\right)\right)}$$

Insert the energies of the five subshells of orbitals in chlorine into this equation and figure out the five Z_{eff}'s

$$Z_{\text{eff}}(1s) \approx \sqrt{1^2\left(\frac{-(-2835\text{ eV})}{13.607\text{ eV Ry}^{-1}}\right)} = 14.4 \quad Z_{\text{eff}}(2s) \approx \sqrt{2^2\left(\frac{-(-273\text{ eV})}{13.607\text{ eV Ry}^{-1}}\right)} = 8.96$$

$$Z_{\text{eff}}(2p) \approx \sqrt{2^2\left(\frac{-(-205\text{ eV})}{13.607\text{ eV Ry}^{-1}}\right)} = 7.76 \quad Z_{\text{eff}}(3s) \approx \sqrt{3^2\left(\frac{-(-21\text{ eV})}{13.607\text{ eV Ry}^{-1}}\right)} = 3.7$$

$$Z_{\text{eff}}(3p) \approx \sqrt{3^2\left(\frac{-(-10\text{ eV})}{13.607\text{ eV Ry}^{-1}}\right)} = 2.6$$

5.32 **a)** Sm **b)** Ca **c)** I^- **d)** Ge e) Rb

5.34 **a)** The two are isoelectronic, and S^{2-} has a lesser nuclear charge; it is larger, **b)** The Tl^+ is larger. Loss of two electrons to give Tl^{3+} reduces electron-electron repulsions and so allows contraction, **c)** The Ce^{3+} ion is larger, considering the lanthanide contraction, **d)** The I^- ion is larger; its outer electrons are in the $n = 5$ shell.

5.36 For both K and Ca, the outer electrons are in the 4*s* shell, outside of the Ar core. K has the lower ionization energy because of its lower nuclear charge. The second 4*s* electron in Ca only partially shields the first. K^+ is isoelectronic with Ar; Ca^+ is isoelectronic with K. Thus the comparison of the ionization energies of K^+ and Ca^+ echoes that of Ar and K. Ca^+ has an appreciably lower ionization energy. In comparing K with Ca^+ *(i.e.,* the first ionization energy of K with the second of Ca), one is comparing isoelectronic species. The one with the higher nuclear charge (Ca^+) has the higher ionization energy.

5.38 The electron affinity of Cl is higher than that of S because Cl^- ion has a closed-shell configuration while S^- does not. The ionization energy of Cl is higher than that of S because the Z_{eff} for the outermost electron is greater in Cl than in S, a consequence of poor shielding of the additional positive charge on the Cl nucleus by the added electron.

5.40 Calcium does have a positive affinity for an electron, but the quoted number is very small. Convert it from kJ mol^{-1} to J per atom and then use $E = hc/\lambda$ to compute the wavelength. Using the most recent value for the *EA* of Ca(2.0 kJ mol^{-1}) gives 6.0×10^{-5} m ; using the earlier value of 1.7 kJ mol^{-1} gives 7.0×10^{-5} m . Infrared radiation is energetic enough to detach the extra electron from Ca^-.

5.42 The lowest excited state of element X is (500 – 120) kJ mol^{-1} above the ground state.

$$\Delta E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\text{ J s})(2.998\times10^{8}\text{ m s}^{-1})}{(500-120)\text{ kJ mol}^{-1}(1/6.022\times10^{23}\text{ mol}^{-1})(10^{3}\text{ J kJ}^{-1})}$$

$$= 3.15\times10^{-7}\text{ m} = 315\text{ nm}$$

5.44 In neutral Li atoms, the two 1*s* electrons screen the attraction between the nucleus and an outermost 2*s* electron less effectively than they screen the attraction between the nucleus and an outermost 2*p* electron. Or, equivalently, a 2*s* electron penetrates the screen imposed by the two 1*s* electrons and approaches the nucleus more effectively than does a 2*p* electron. Either way, the 2*s* electron is lower in energy than the 2*p*. The Li^{+2} ion has no inner electrons. The energies of a 2*s* and 2*p* electron are governed (almost) exclusively by the principal quantum number *n* and are thus (almost) the same. The very slight difference mentioned in the problem comes from differing relativistic perturbations on the motion of the electron in the two states and differences in the spin-orbit coupling in the two states.

5.46 The probability of finding an electron in an element of volume surrounding a point in space is proportional to the square of the electron's wave-function evaluated at that point. For the 1*s* electron in hydrogen

$$\psi_{1s}^2 = \frac{1}{\pi a_0^3}\exp\left(-2r / a_0\right)$$

This ψ_{1s}^2 has units of reciprocal volume (m^{-3}). For example, $\psi_{1s}^2\left(r=0\right)$ equals $2.15\times10^{30}\ \text{m}^{-3}$. To obtain an actual probability, a ψ^2 must to be multiplied by the size of the volume element surrounding the point, not just evaluated at that point. This gives a pure number, as required for a probability (because $\text{m}^{-3}\times\ \text{m}^3=1$. The probability of finding the electron *exactly at* a mathematical point is zero because a point has no volume to accommodate the electron.

a) The small sphere centered at the nucleus of the H atom has a volume of 1 pm^3 $\left(1.0\times10^{-36}\ \text{m}^3\right)$. Over the very short distance between the center and surface of this sphere, ψ^2 stays nearly constant at $2.15\times10^{30}\ \text{m}^{-3}$, and

$$\text{probability} = \left(2.15\times10^{30}\ \text{m}^{-3}\right)\times\left(1.00\times10^{-36}\ \text{m}^3\right) = 2.15\times10^{-6}$$

b) At r = 52.9 pm $\left(r=a_0\right)$, ψ_{1s}^2 evaluates to *less* than at r = 0:

$$\psi_{1s}^2\left(r=a_o\right) = \left(2.15\times10^{30}\ \text{m}^{-3}\right)\text{e}^{-2} = 2.91\times10^{29}\ \text{m}^{-3}$$

Assume that ψ_{1s}^2 is constant throughout the 1 pm^3 volume that the problem specifies. The chance of finding the electron at 52.9 pm in a fixed direction is

$$\text{probability} = \left(2.91\times10^{29}\ \text{m}^{-3}\right)\left(1.0\times10^{-36}\ \text{m}^3\right) = 2.91\times10^{-7}$$

c) A spherical shell of thickness 1 pm and radius 52.9 pm has a volume

$$V_{\text{shell}} = 4\pi r^2\Delta r = 4\pi\left(52.9\ \text{pm}\right)^2\left(1\ \text{pm}\right) = 3.52\times10^{-32}\ \text{m}^3$$

This larger volume (35200 pm^3) is more likely to contain the electron than the tiny 1 pm^3 volume element considered in part **b**)

$$\text{probability} = \left(2.91\times10^{29}\ \text{m}^{-3}\right)\left(3.52\times10^{-32}\ \text{m}^3\right) = 0.0102$$

The wave-function usually changes its value significantly within volume elements of interest. In the most general case, a triple integration of the wave-function is required. In spherical coordinates

$$\text{probability} = \int_r \int_\theta \int_\varphi \psi^2(r,\theta,\varphi)\ r^2 \mathrm{d}r\ \sin\theta \mathrm{d}\theta\ \mathrm{d}\varphi$$

where the limits of the integration define the size and shape of the volume element.

5.48 **a)**

$$Y(px) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\ \cos\varphi \quad Y(py) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\ \sin\varphi \quad Y(pz) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

The radial parts of the wave functions need not be taken into account because they do not affect the angular symmetry.

$$\begin{aligned} Y^2(px) + Y^2(py) + Y^2(pz) &= \left(\frac{3}{4\pi}\right) \left(\sin^2\theta\cos^2\varphi + \sin^2\theta\sin^2\varphi + \cos^2\theta\right) \\ &= \left(\frac{3}{4\pi}\right) \left(\sin^2\theta\left(\cos^2\varphi + \sin^2\varphi\right) + \cos^2\theta\right) \\ &= \left(\frac{3}{4\pi}\right) \left(\sin^2\theta(1) + \cos^2\theta\right) = \frac{3}{4\pi} \end{aligned}$$

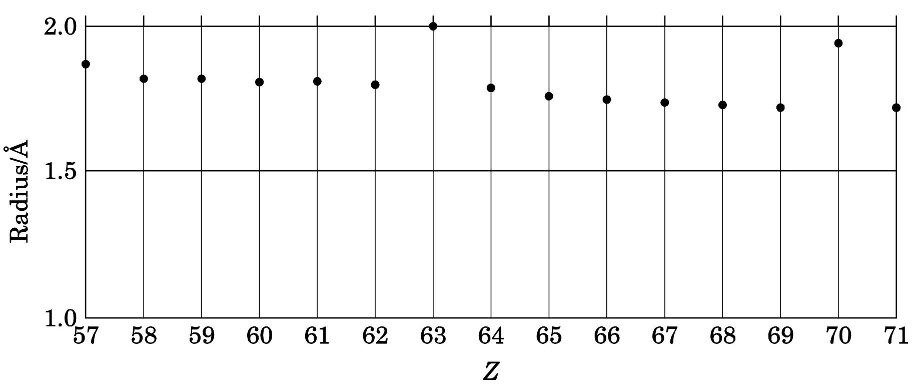
The N atom is spherically symmetric because ψ^2 is independent of θ and φ.

b) The following species are spherically symmetric: F^-, Na, S^{2-}, Cu, Mo, Sb, Au.

5.50 **a)** The trend in atomic radius with Z for the rare earth elements is generally downward (the so-called lanthanide contraction). It is caused by the increasing nuclear charge that attracts the electrons in the 4*f* sub-shell toward the nucleus.

b) The elements 63(Eu) and 70(Yb) are the exceptions to the trend. They contain, respectively, a half-filled and a filled 4*f* sub-shell.

Atomic Radii of the Lanthanides



5.52 The third ionization energy of Li is the ΔE for the process $Li^{2+}(g) \rightarrow Li^{3+}(g) + e^-$. The ejection of a 1*s* electron from a lithium atom on the other hand is represented $Li(g) \rightarrow Li^{+*}(g) + e^-$. where the star indicates that the Li^+ ion is in an excited state. In both cases a 1*s* electron is removed. The IE_3 is larger because the 1*s* electron is removed against the full attraction of the Z = 3 nucleus whereas the removal of the 1*s* electron in the photoelectron spectroscopy experiment is assisted by repulsions from the other two electrons.

5.54 Two photons must furnish at least 419 kJ mol^{-1} to a K atom. The wavelength of the first is known, but not the wavelength of the second. The energy of each is given by hc/λ, so

$$\frac{hc}{\lambda_1}+\frac{hc}{\lambda_2}\geq 419\times10^3 \text{ J mol}^{-1}$$

$$\frac{1}{\lambda_1}+\frac{1}{\lambda_2}\geq\frac{(419\times10^3 \text{ J mol}^{-1})(10^{-9} \text{ m nm}^{-1})}{(6.626\times10^{-34} \text{ J s})(2.9979\times10^8 \text{ m s}^{-1})(6.022\times10^{23} \text{ mol}^{-1})}$$

$$\frac{1}{650 \text{ nm}}+\frac{1}{\lambda_2}\geq 0.003502 \text{ nm}^{-1}$$

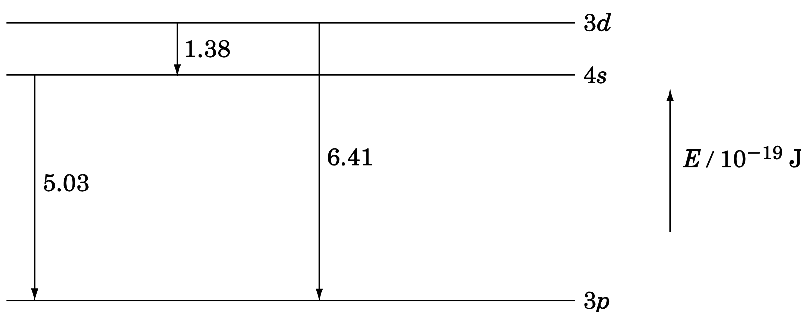
$$\lambda_2\leq 509 \text{ nm}$$

5.56 **a)** Ground-state Al: $1s^22s^22p^63s^23p^1$.

b)

$$\Delta E=\frac{hc}{\lambda}=\frac{(6.626\times10^{-34} \text{ J s})(2.998\times10^8 \text{ m s}^{-1})}{395\times10^{-9} \text{ m}}=5.03\times10^{-19} \text{ J}$$

c) The energy level diagram for Al



The separation is 1.38×10^{-19} J, the $3d$ state lying above the $4s$ state.

Chapter 6

Quantum Mechanics and Molecular Structure

6.2 Text Figure 6.5 diagrams constant-amplitude contours for the eight lowest-energy MO's of the H_2^+ ion. Two of these are π MO's: the $1\pi_u$ and the $1\pi_g^*$.

Columns (a) and (b) of the figure show the nodes of these MO's. Nodes are surfaces at which the wave-function y changes sign. The contour plots show that the $1\pi_u$ MO has one node, a plane that coincides with the *xz* plane. This node *contains* the internuclear axis (the *z* axis), but it is not crossed when moving along the *z* axis. Thus, the $1\pi_u$ MO has zero nodes "along" the internuclear axis.

The $1\pi_g^*$ MO has two nodal planes, the *xz* plane and the *xy* plane. The *xz* plane contains the internuclear axis; the *xy* plane is crossed at $z = 0$ when moving along the internuclear axis. The $1\pi_g^*$ MO thus has one node "along" the *z* axis.

Both of these π wave-functions equal zero at all points *on* the internuclear axis.

6.4 Text Figure 6.5 diagrams constant-amplitude contours for the eight lowest-energy MO's of the H_2^+ ion. Two of these are π MO's, the $1\pi_u$ and $1\pi_g^*$.

The *xy* plane bisects the distance between the two H nuclei. A cross-section of constant-amplitude surfaces of the $1\pi_u$ MO in this plane looks like two flattened ellipses, one above the *xz* plane (this plane is being viewed edge-on) and the other below it. The look is similar to text Figure 5.7. In a plane parallel to the *xy* plane at $z = \frac{1}{4}$ (or $\frac{3}{4}$), the shape of the $1\pi_u$ MO is the same (two flattened ellipses), but the amplitudes are less than at points having the same values of *x* and *y* and $z = 0$.

The $1\pi_g^*$ MO has two nodal planes, the *xz* plane and the *xy* plane. Because the $1\pi_g^*$ MO has zero amplitude in the *xy* plane, a sketch of constant-amplitude contours in this plane contains all zeroes (has no contours).

In the plane parallel to the *xy* plane but at $\frac{1}{4}$ (or $\frac{3}{4}$) of the distance between the H nuclei instead of $\frac{1}{2}$ the distance, the cross-section of constant-amplitude surfaces again looks like two flattened ellipses, one above the *xz* plane (which is a node being viewed edge-on) and one below. The amplitude of the $1\pi_g^*$ MO, is less than the amplitude of the $1\pi_u$ MO at all points in this plane having non-zero amplitude.

6.6 The $1\sigma_g$ MO is the ground state in H_2^+ because it puts the most electron probability density in the region between the two H nuclei. This leads to strong e^- to H^+ attractions to overcome the H^+ to H^+ repulsion. An electron in any other bonding σ MO's, such as the $2\sigma_g$ MO, is generally further away from the nuclei and so spends less time in the region between the nuclei. This describes a situation of higher energy (bound but excited). The bonding π MO's are also less well localized between the nuclei than the $1\sigma_g$. These orbitals all equal zero at all points on the internuclear axis. Conclusion: the MO description of the bond in H_2^+ ion is consistent with the classical model, but improves on it by explaining the existence of excited molecular states.

6.8 The ground state electron configuration of the He^{2+} ion is $(\sigma_{1s})^2$ with bond order one. This configuration is stable in its ground state.

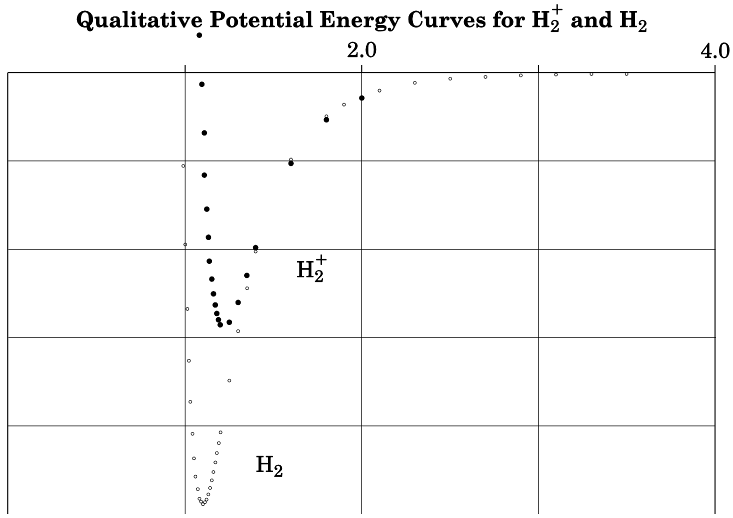
De-Localized Bonds: Molecular Orbital Theory and the LCAO Approximation

6.10 Ground-state H_2 has two electrons in bonding MO's (configuration: $(\sigma_{g1s})^2$); ground-state H_2^+ has one electron in a bonding MO (configuration: $(\sigma_{g1s})^1$. H_2 has a bond order of 1; H_2^+ has a bond order of $1/2$: H_2 has the larger bond energy.

6.12 The species H_2^+ has a longer bond distance because it has a lower bond order (see problem **6.10**).

6.14 The sketch graph of the potential energy curve for H_2^+ should have a shallower minimum at a longer internuclear distance that the one for H_2.

Qualitative Potential Energy Curves for H_2^+ and H_2



6.16 Ground-state He_2^+ gives ground-state He_2^{2+} when the most weakly bound electron is removed. The electron comes from an anti-bonding MO. The resulting He_2^{2+} ion accordingly has a greater bond energy and a shorter bond length than He_2^+.

6.18 **a)** The qualitative correlation diagram for O_2^- is identical to the diagram given for F_2 in text Figure 6.17b except that an electron is removed from either the π^*_{2px} or the π^*_{2py} level.

b) The ground-state electron configuration of O_2 is listed in Table 6.3. Derive the configurations of the ions in the problem by removal of electrons from the highest occupied or addition to the lowest unoccupied molecular orbitals:

$$O_2^+: \left(\sigma_{g2s}\right)^2\left(\sigma^*_{u2s}\right)^2\left(\sigma_{g2pz}\right)^2\left(\pi_{u2p}\right)^4\left(\pi^*_{g2p}\right)^1 \qquad O_2: \left(\sigma_{g2s}\right)^2\left(\sigma^*_{u2s}\right)^2\left(\sigma_{g2pz}\right)^2\left(\pi_{u2p}\right)^4\left(\pi^*_{g2p}\right)^2$$
$$O_2^-: \left(\sigma_{g2s}\right)^2\left(\sigma^*_{u2s}\right)^2\left(\sigma_{g2pz}\right)^2\left(\pi_{u2p}\right)^4\left(\pi^*_{g2p}\right)^3 \qquad O_2^{2-}: \left(\sigma_{g2s}\right)^2\left(\sigma^*_{u2s}\right)^2\left(\sigma_{g2pz}\right)^2\left(\pi_{u2p}\right)^4\left(\pi^*_{g2p}\right)^4$$

c) The bond orders of the species are $\frac{5}{2}$ (for O_2^+), 2 (for O_2), $\frac{3}{2}$ (for O_2^-) and 1 (for O_2^{2-}).

b) All of the species except O_2^{2-} should be paramagnetic. A species with an odd number of electrons is automatically paramagnetic. The reason for the paramagnetism of ordinary O_2 is discussed in the text.

c) Members of the series O_2^+ through O_2^{2-} are differentiated by successive addition of an electron. Each electron goes into a π^* antibonding orbital. The bond dissociation energy decreases along the series.

6.20 It is unnecessary to show the configurations for core electrons in I_2, which play little part in bonding. Then:

$$I_2: \left(\sigma_{g5s}\right)^2\left(\sigma^*_{u5s}\right)^2\left(\sigma_{g5pz}\right)^2\left(\pi_{u5p}\right)^4\left(\pi^*_{g5p}\right)^4$$ This substance is diamagnetic.

6.22 **a)** X_2: $\left(\sigma_{g2s}\right)^2\left(\sigma^*_{u2s}\right)^2\left(\sigma_{g2p}\right)^2\left(\pi_{u2p}\right)^4\left(\pi^*_{g2p}\right)^2$: O_2. Bond order: 2.

b) Q_2^-: $\left(\sigma_{g2s}\right)^2\left(\sigma^*_{u2s}\right)^2\left(\sigma_{u2p}\right)^3$: B_2^-. Bond order: $\frac{3}{2}$.

c) Z_2^{2+}: $\left(\sigma_{g2s}\right)^2\left(\sigma^*_{u2s}\right)^2\left(\sigma_{g2p}\right)^2\left(\pi_{u2p}\right)^4\left(\pi^*_{g2p}\right)^2$: F_2^{2+}. Bond order: 2.

6.24 **a)** paramagnetic **b)** paramagnetic **c)** paramagnetic

6.26 Follow the pattern shown in text Figure 6.19. The nitrogen atomic orbitals are lower in energy than the corresponding beryllium orbitals because N is more electronegative than Be. The BeN molecule has 7 valence electrons in the ground-state configuration: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_2)^3$. Its bond order is $\frac{3}{2}$. BeN is paramagnetic.

6.28 The nitrosyl ion NO^+ forms from nitric oxide (NO) by the loss of an electron from the highest occupied molecular orbital. The ground-state valence electron configuration of NO is $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2pz})^2(\pi^*_{2p})^1$ so the electron comes from a π^*_{2p} orbital. Because this is an antibonding orbital, the bonding in NO^+ should be stronger and the bond should be shorter than in NO. Also, NO^+ should be diamagnetic.

6.30 The HeH^+ ion has the electron configuration $(\sigma_{1s})^2$. Its bond order is 1, and it is diamagnetic. The lower energy state should be reached by the reaction $HeH^+ \rightarrow He + H^+$. This set of products is more stable than He^+ + H because in it the two electrons are both close to the 2+ charge of the helium nucleus instead of the 1+ charge of the hydrogen nucleus and very roughly the same distance from each other.

6.32 The ground state electron configuration of HeBe is predicted to be $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2$ with bond order one.

6.34 The ground state electron configuration of CO is $(\sigma_{2s})^2(\sigma_{2s}^*)(\pi_{2p_x}, \pi_{2p_y})^4(\pi_{2p_z})^2$ and the ground state electron configuration of NO is $(\sigma_{2s})^2(\sigma_{2s}^*)(\pi_{2p_x}, \pi_{2p_y})^4(\pi_{2p_z})^2(\pi_{2p_{x,y}}^*)^1$. The highest energy occupied orbital in NO is $(\pi_{2p_{x,y}}^*)$ which is much higher in energy than the highest energy occupied orbital in CO, (π_{2p_z}) thus accounting for the greater ionization energy of CO.

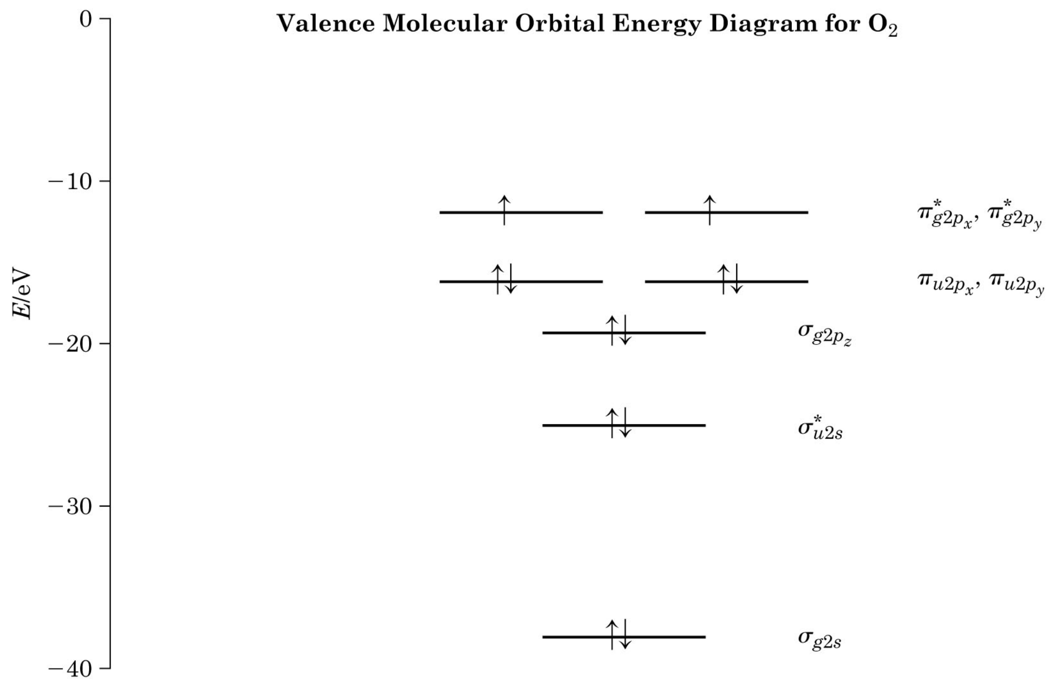
Photoelectron Spectroscopy for Molecules

6.36 High-energy x-radiation hits molecules of O_2 and ejects electrons

$$
\begin{aligned}
IE &= h\nu_{\text{photon}} - \tfrac{1}{2} m_e \upsilon^2 \\
&= 1253.6\ \text{eV} - \frac{\tfrac{1}{2}\left(9.109\times10^{-31}\ \text{kg}\right)\left(1.57\times10^{7}\ \text{m s}^{-1}\right)^2}{1.60218\times10^{-19}\ \text{J e V}^{-1}} \\
&= 1253.6\ \text{eV} - 700.7\ \text{eV} = 553\ \text{eV}
\end{aligned}
$$

From text Figure 6.34 (page 279), these electrons must have been ejected from the σ_{g1s} orbital of O_2, which has an ionization energy of approximately 543 eV.

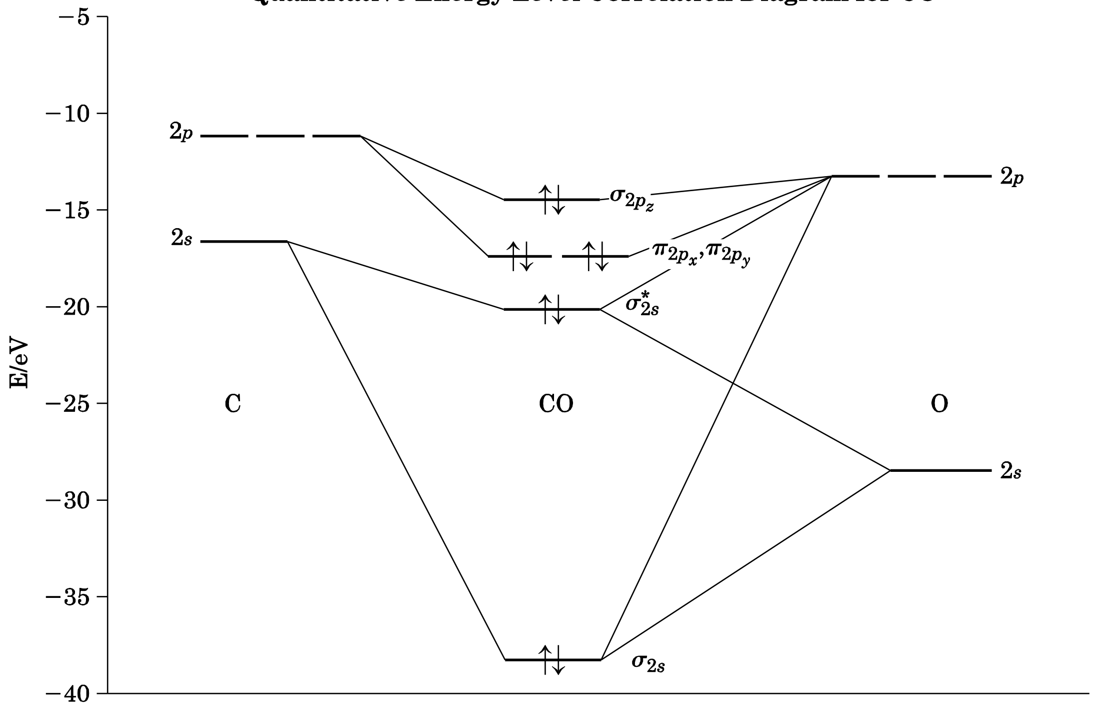
6.38 Look in text page 267 for data. The n = 0 peak in each labelled group of peaks is the one at lowest energy. Read the graph to obtain these energies: $\pi^*_{g2p_x}$ and $\pi^*_{g2p_y}$ at 12.1 eV; π_{u2p_x} and π_{u2p_y} at 16.1 eV; σ_{g2pz} at 19.3 eV; σ^*_{u2s} at 25.0 eV; σ_{g2s} at 38.0 eV. The energy of the σ_{g2pz} MO is the average of 18.2 and 20.4 eV, which are the energies of n = 0 peaks in the two groups of peaks in text page 267 having this label. The photoelectron experiment does not reveal the energy of the σ^*_{u2pz} MO, which appears in text Figure 6.17b. because this MO is unoccupied in ground-state O_2. It consequently does not appear in the diagram.



6.40 Model the correlation diagram after text Figure 6.20. Make the diagram quantitative by positioning both the atomic and molecular orbitals on the vertical scale according to their energies. The carbon atom's 2*p* and 2*s* orbitals have energies of −11.26 eV and −16.59, respectively. The first of these energies is given in the problem. It is the first ionization energy of the neutral carbon atom. The second can be looked up in the chemical literature or estimated from the location of $Z = 6$ dot on the blue 2*p* line in text Figure 5.21. The valence orbitals of oxygen are at lower energy than those of carbon because the nuclear charge of oxygen exceeds the nuclear charge of carbon but the orbitals are in the same $n = 2$ shell. Their energies are −13.26 eV (for the 2*p)* and −28.48 eV (for the 2*s*).

The following correlation diagram shows eight atomic orbitals but only five molecular orbitals. The $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ and the $\sigma^*_{2p_z}$ MO's do not appear at the top of the diagram because their energies are not attainable from the photoelectron spectroscopy experiment.

Quantitative Energy Level Correlation Diagram for CO



6.42 The valence-electron configuration of B is $2s^2\ 2p^1$. The valence-bond (VB) wave-functions for diboron B_2 are constructed by overlap of the half-filled $2p$ orbital on the first boron (atom A) and the half-filled $2p$ orbital on the second boron (atom B):

$$\psi_\sigma^{\text{bond}}\left(1,2;R_{\text{AB}}\right)=C_1\left(R_{\text{AB}}\right)\left[2p^{\text{A}}\left(1\right)2p^{\text{B}}\left(2\right)+2p^{\text{A}}\left(2\right)2p^{\text{B}}\left(1\right)\right]$$

Combining the two functions in the brackets on the right using a minus instead of a plus sign (the *ungerade* combination) gives repulsion between the atoms at all distances. The LCAO approach (summarized in text Table 6.6) also predicts a single bond.
The valence-electron configuration of O is $2s^2\ 2p^4$. Overlap of a half-filled $2p$ orbital (call it the $2p_z$) on oxygen A with the half-filled $2p_z$ orbital on oxygen B gives a *s* bond

$$\psi_\sigma^{\text{bond}}\left(1,2;R_{\text{AB}}\right)=C_1\left(R_{\text{AB}}\right)\left[2p_z^{\text{A}}\left(1\right)2p_z^{\text{B}}\left(2\right)+2p_z^{\text{A}}\left(2\right)2p_z^{\text{B}}\left(1\right)\right]$$

The other half-filled $2p$ orbitals on oxygen A and B can overlap laterally to form a π bond

$$\psi_\pi^{\text{bond}}\left(1,2;R_{\text{AB}}\right)=C_2\left(R_{\text{AB}}\right)\left[2p_x^{\text{A}}\left(1\right)2p_x^{\text{B}}\left(2\right)+2p_x^{\text{A}}\left(2\right)2p_x^{\text{B}}\left(1\right)\right]$$

Both the VB approach and the MO approach (in text Table 6.3) predict a double bond in the O_2 molecule.

6.44 The VB approach finds no possibility of overlap for the orbitals in Ne atoms because they are all filled (configuration $2s^22p^6$). Excitation of electrons into higher-energy shells would use an unacceptably large amount of energy. The MO approach finds that the number of electrons in bonding MO's equals the number of electrons in anti-bonding MO's, leading to a non-bonding situation.

6.46 The simple VB model predicts that C (valence electron configuration $2s^22p_x^12p_y^1$) and H (valence electron configuration $1s^1$) will form the bent molecule H—C—H with two bonds at a 90° angle arising from overlap of the half-filled orbitals. The two valence-bond wave-functions are

$$\text{C—H}_1\quad \psi_\sigma^{\text{bond}}\left(1,2;R_{\text{CH}_1}\right)=c_1\left[1s^{\text{H}_1}\left(1\right)2p_x^{\text{C}}\left(2\right)\right]+c_2\left[1s^{\text{H}_1}\left(2\right)2p_x^{\text{C}}\left(1\right)\right]$$
$$\text{C—H}_2\quad \psi_\sigma^{\text{bond}}\left(1,2;R_{\text{CH}_2}\right)=c_1\left[1s^{\text{H}_2}\left(1\right)2p_y^{\text{C}}\left(2\right)\right]+c_2\left[1s^{\text{H}_2}\left(2\right)2p_y^{\text{C}}\left(1\right)\right]$$

The correct prediction is CH_4. Modified (not so simple) VB theory invokes hybridization to overcome the difficulty, as explained on text page 272.

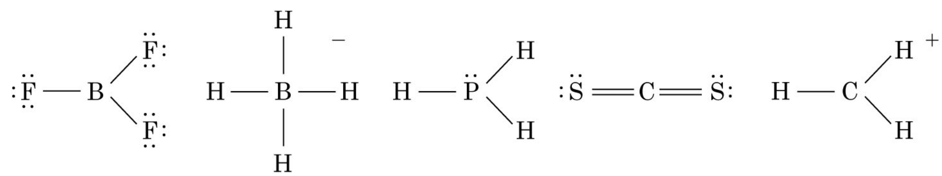
6.48 The simple VB model predicts that O (valence electron configuration $2s^22p_x^12p_y^12p_z^2$) forms single bonds with each of the two H atoms. These atoms are designated H_1 and H_2 in the following valence-bond wave functions, which come from overlap of the $2p_x$ and $2p_y$ orbitals on the O with the respective $1s$ orbitals on the H's

$$\text{O—H}_1\quad \psi_\sigma^{\text{bond}}\left(1,2;R_{\text{OH}_1}\right)=c_1\left[1s^{\text{H}_1}\left(1\right)2p_x^{\text{O}}\left(2\right)\right]+c_2\left[1s^{\text{H}_1}\left(2\right)2p_x^{\text{O}}\left(1\right)\right]$$
$$\text{O—H}_2\quad \psi_\sigma^{\text{bond}}\left(1,2;R_{\text{OH}_2}\right)=c_1\left[1s^{\text{H}_2}\left(1\right)2p_y^{\text{O}}\left(2\right)\right]+c_2\left[1s^{\text{H}_2}\left(2\right)2p_y^{\text{O}}\left(1\right)\right]$$

The model predicts (incorrectly) that the H—O—H angle equals 90°.

6.50 The central O in H_3O^+ has $SN = 4$. Assume sp^3 hybridization on a central O^+ ion. One of the four hybrid orbitals is filled. The other three are half-filled and overlap with 1*s* orbitals from three H atoms. The resulting H_3O^+ will be pyramidal.

6.52 The Lewis structures are



a) The central B in BF_3 has $SN = 3$. It is sp^2 hybridized, and the molecule is trigonal-planar.

b) The central B in BH_4^- has $SN = 4$. It is sp^3 hybridized, and the molecular ion is tetrahedral.

c) The central P in PH_3 has $SN = 4$. It is sp^3 hybridized, and the molecule is pyramidal.

d) The central C in CS_2 has $SN = 2$. It is *sp* hybridized, and the molecule is linear.

e) The central C in CH_3^+ has $SN = 3$. It is sp^2 hybridized, and the molecular ion is trigonal-planar.

6.54 The tetrahedral ClO_4^- ion uses sp^3 hybrid orbitals on the central Cl atom (which has $SN = 4$). The pyramidal ClO_3^- also uses sp^3 hybrid orbitals on the central CI atom (which still has $SN = 4$).

6.56 The carbon atom in N≡C—Cl has a steric number of 2. It is *sp* hybridized, and the molecule should be linear.

6.58 The OF_2 molecule has 20 valence electrons. Two O—F *s* bonds form from overlap of sp^2 hybrid orbitals on the central O atom with 2*p* orbitals on the two F atoms. These two bonds use four electrons. Ten electrons occupy orbitals that are not properly oriented for overlap with other atoms' orbitals: two in the 2*s* orbital on F1; two in a 2*s* orbital on F2; two in the 2*p* orbital on Fl, two in a 2*p* orbital on F2; two in the third sp^2 hybrid orbital on the O. This leaves six electrons and three *p* orbitals (one each on three atoms). These *p* orbitals overlap to form the π molecular orbital system shown in Text Figure 6.27. The resulting MO's accommodate electrons as follows: $(\pi)^2(\pi^{nb})^2(\pi^*)^2$. The bond order of the molecule based on just the *s* bonding is 2. The π system adds nothing to this. For this reason the bonding in OF_2 can also be described as the result of σ overlap of sp^3 hybrid orbitals on the central O atom with 2*p* orbitals on the two F atoms and the assignment of the other 16 electrons to lone pairs (three of them on each F and two on the O).

6.60 For NO_2^+, *sp* hybrid orbitals on the central N atom form two σ-bonds with p_z orbitals on outer oxygen atoms (4 electrons).

Lone pair 2*s* orbitals on outer oxygens (4 electrons).

π_x, π_y, π_x^{nb} and π_y^{nb} each with 2 electrons.

Linear and not paramagnetic.

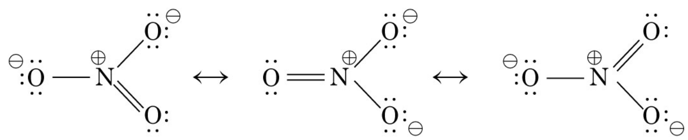
For NO_2 and NO_2^-, sp^2 hybrid orbitals on the central N atom form form two σ-bonds with outer oxygen 2*p* orbitals and one with a lone pair on N (6 electrons).

Lone pair 2*s* and 2*p* orbitals on outer atoms (8 electrons).

π orbital containing 1 (NO_2) or $2\left(NO_2^-\right)$ electrons.

Both are non-linear, but only NO_2 is paramagnetic.

6.62 The nitrate ion has 24 valence electrons. Three resonance structures are needed to represent the equivalence of the three N to O bonds:



The *SN* of the central nitrogen is 3, which in VSEPR theory predicts trigonal-planar geometry about the central nitrogen. This corresponds to sp^2 hybridization of the valence orbitals of the central N. Six valence electrons are shared between the N and the O's in these orbitals. The remaining 2*p* orbital of the nitrogen combines with one 2*p* orbital on each of the three oxygen atoms to form a set of four π molecular orbitals. The lowest lying of these, a bonding orbital, is occupied by a pair of electrons. The net effect is that the four atoms are bonded by eight electrons: each of the three links between N and O has bond order 4/3.

6.64 The carbide ion has 10 valence electrons; $(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^4(\sigma_{g2pz})^2$ is its ground-state configuration. This is the same as the configuration of N_2. Its bond order is 3.

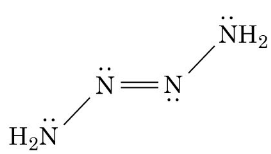
6.66 The ground-state electron configuration of Be_2 is $(\sigma_{g2s})^2(\sigma^*_{u2s})^2$. The predicted bond order of the molecule is zero, and according to simple theory it should not exist. The observed bond length and dissociation enthalpy of Be_2 are respectively high and quite low: the molecule indeed almost does not exist.

6.68 The electron configuration in HeH^+ is $\left(\sigma_{1s}\right)^2$ with the 1*s* orbital from He lying lower in energy than the 1*s* orbital from H. The constant C_2 exceeds C_1 because the electron is more strongly attracted to the doubly positive He^{2+} nucleus.

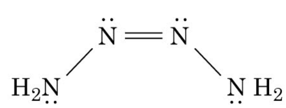
6.70 The cyclic H_3^+ molecular ion is a perfect equilateral triangle. It has two electrons. The electrons are in a low-energy bonding orbital mainly localized in the center of the triangle so as best to offset internuclear repulsions.

6.72 *Trans*-tetrazene and *cis*-tetrazene have the structures:

trans



cis



The *SN*'s of all nitrogen atoms in both structures are 3. There is sp^2 hybridization at all nitrogen atoms, and the molecules are planar, except for the terminal hydrogen atoms, because of the π system

Chapter 7

Bonding in Organic Molecules

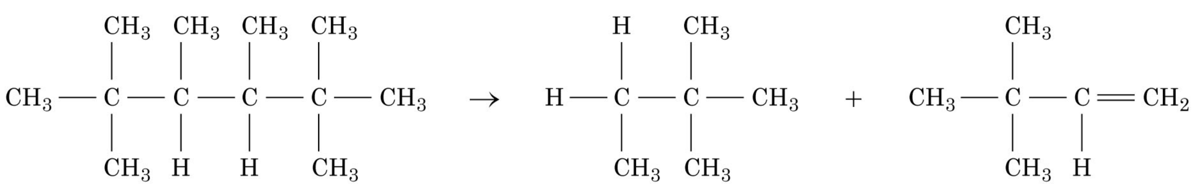
7.2 Yes. The gasoline would knock worse in an engine than *n*-heptane.

7.4 Alkynes (more strictly, monoalkynes) have the general formula C_nH_{2n-2}. They burn accordingly to the partially balanced equation

$$C_nH_{2n-2}(g) + O_2(g) \rightarrow CO_2(g) + \tfrac{2n-2}{2}H_2O(g)$$

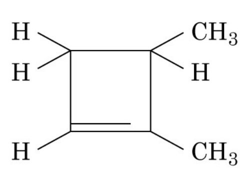
Let the coefficient of C_nH_{2n-2} in this equation equal 1. The statement of the problem requires, in accord with Avogadro's principle, that $(2n-2)/2$, the coefficient of H_2O, also equal 1. It follows that $n = 2$. The alkyne must therefore be C_2H_2, ethyne (acetylene). The balanced equation is $C_2H_2(g) + \tfrac{5}{2}O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g)$.

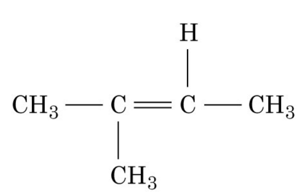
7.6 **a)** The catalytic cracking reaction is



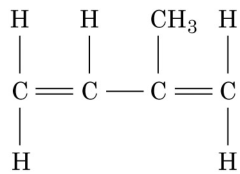
b) There are 16 isomers to choose from: three butenes, eight pentenes, and five hexenes. The butenes are 3,3-dimethyl-1-butene (shown in part **a**)) 2,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene. The pentenes consists of three 1-pentenes (2-methyl-1-pentene, 3-methyl-1-pentene and 4-methyl-1-pentene) and five 2-pentenes (2-methyl-2-pentene, 3-methyl-2-pentene and 4-methyl-2-pentene). The last two named exist in *cis* and *trans* forms. The five hexenes are 1-hexene, 2-hexene, and 3-hexene of which the latter two exist in *cis* and *trans* forms.

7.8 The structural formulas are

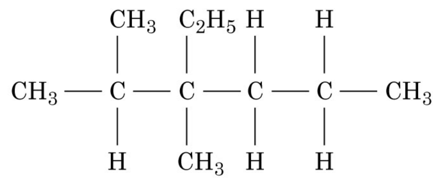
a) 

b) 

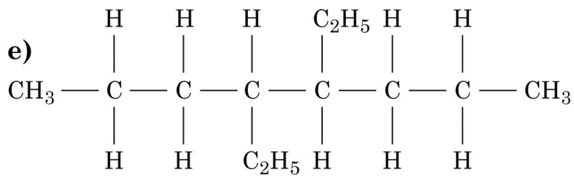
c)



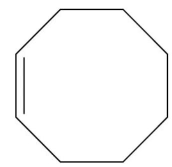
d)



e)



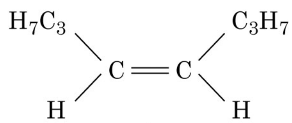
f)



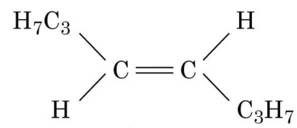
g) $H_2C=C=CH_2$

h) $CH_3—CH_2—C\equiv C—CH_3$

7.10 The isomers of 4-octene are



cis



trans

7.12 **a)** 2,3-dimethyl-1,3-butadiene **b)** 2,4-hexadiene **c)** 2,2-dimethylbutane **d)** methylpropene

7.14 **a)** The two $—CH_3$ carbons are sp^3, and the other four are sp^2 hybridized.
b) The two $—CH_3$ carbons are sp^3, and the other four are sp^2 hybridized.
c) All are sp^3 hybridized.
d) The two $—CH_3$, carbons are sp^3, and the other two are sp^2 hybridized.

7.16 **a)** $C_{12}B_{24}N_{24}$ has the same number of valence electrons as C_{60}.

b) The C_{60} molecule (see text Figure 7.18) has 32 faces, 60 vertices and 90 edges. Twelve of its faces are pentagons; the other 20 are hexagons. To make the most symmetrical possible $C_{12}B_{24}N_{24}$, replace 48 C's with 24 B's and 24 N's in such a way that no B's adjoin B's (along an edge) and no N's adjoin N's. Make sure that each pentagon retains exactly 1 C that is bonded to a C on another pentagon. When this is done, six C—C bonds remain to link the 12 pentagons in 6 distinct pairs. The new molecule has 60 B—N linkages, 12 C—B linkages, 2 C—N linkages and 6 C—C linkages. Half of the B—N linkages are double bonds.

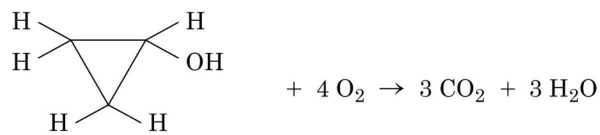
7.18 Compute the amount of ethylene dichloride required to make the 3.73×10^9 kg (3.73 Tg) of vinyl chloride. It is clear without writing an equation that the molar ratio of the vinyl chloride to the ethylene dichloride is 1 to 1. Also, 1 mol of HCl is produced for every 1 mol of vinyl chloride. Then

$$m_{C_2H_4Cl_2} = 3.73 \text{ Tg } C_2H_3Cl \times \frac{1 \text{ Tmol } C_2H_3Cl}{62.50 \text{ Tg } C_2H_3Cl} \times \frac{1 \text{ Tmol } C_2H_4Cl_2}{1 \text{ Tmol } C_2H_3Cl} \times \frac{98.96 \text{ Tg } C_2H_4Cl_2}{1 \text{ Tmol } C_2H_4Cl_2}$$
$$= 5.91 \text{ Tg} = 5.91 \times 10^9 \text{ kg}$$

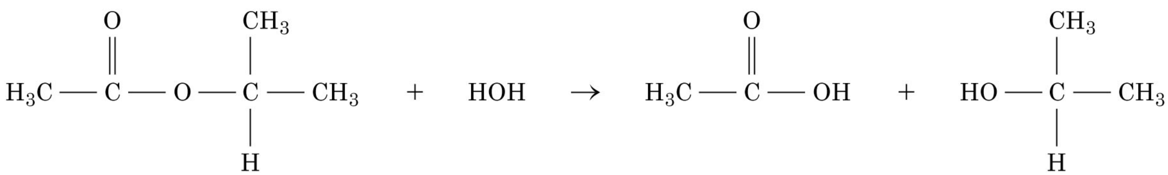
This is 94.3% of the total production of ethylene dichloride. The mass of by-product HCl is 5.91 - 3.73 Tg = 2.18 Tg = 2.18×10^9 kg.

7.20 **a)**

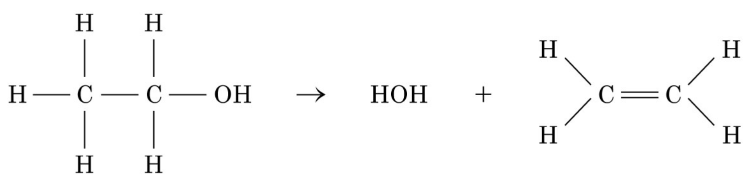
a)



b)



c)



d) $CH_3CH_2CH_2CH_2I + H_2O \rightarrow CH_3CH_2CH_2CH_2OH + HI$

7.22 **a)** React acetic acid, ethylene, and oxygen in the presence of a catalyst

$$CH_3COOH + CH_2CH_2 + \tfrac{1}{2}O_2 \rightarrow CH_3COOCHCH_2 + H_2O$$

b) React formic acid and ammonia

$$HCOOH + NH_3 \rightarrow HCO(NH_2) + H_2O$$

c) React ethylene with fluorine

$$H_2CCH_2 + F_2 \rightarrow FCH_2CH_2F$$

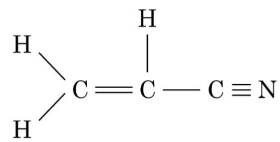
7.24 A tertiary amine has no hydrogen atoms on the nitrogen atom. Hence, it cannot contribute hydrogen to a water molecule as primary and secondary amines do when they condense with a carboxylic acid.

7.26 Compute the chemical amount of hydrogen that is used to saturate the oleic acid

$$n_{H_2} = \frac{PV_{H_2}}{RT} = \frac{(1.00\text{ atm})(4.20\text{ L})}{(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})} = 0.172\text{ mol}$$

The mass of the stearic acid is the mass of the oleic acid, 48.5 g, plus the mass of the hydrogen that it absorbed during the hydrogenation. The mass of the H_2 is 0.172 mol × 2.016 g mol^{-1} = 0.347 g. There is therefore 48.8 g of stearic acid. The molar mass of stearic acid ($C_{18}H_{36}O_2$) is 284.48 g mol^{-1}, so the chemical amount of the stearic acid is 0.172 mol. So 0.172 mol of H_2 was absorbed by the oleic acid for every 0.172 mol of stearic acid produced. a 1 : 1 ratio. The formula of the oleic acid is therefore the formula of stearic acid minus 2 H's: $C_{18}H_{34}O_2$. There is one double bond in oleic acid.

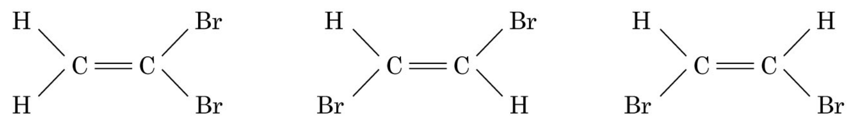
7.28 The structure of acrylonitrile is



The molecule is planar with the six bond angles at the two double-bonded carbon atoms (both sp^2-hybridized) all close to 120° and the bond angle at the triple-bonded C atom (*sp*-hybridized) equal to 180°. The *p* orbitals perpendicular to the molecular plane form a π-bonding system with 4 electrons resembling that in butadiene. The other two *p* orbitals on the *sp*-hybridized C atom and the N atom form an additional doubly occupied π orbital.

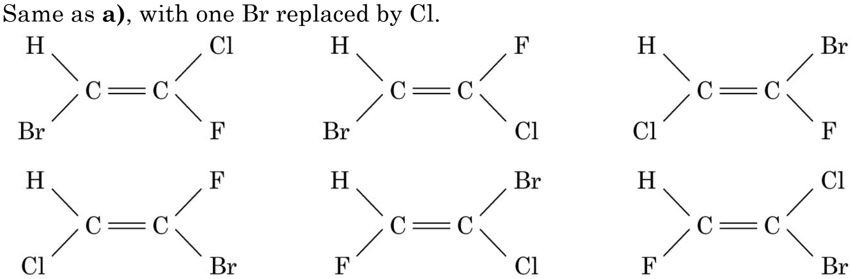
7.30

a)

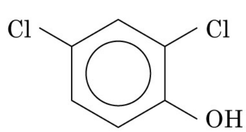


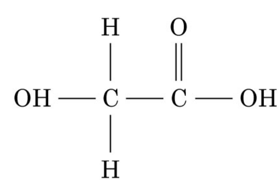
b) Same as **a)**, with one Br replaced by Cl.

c)



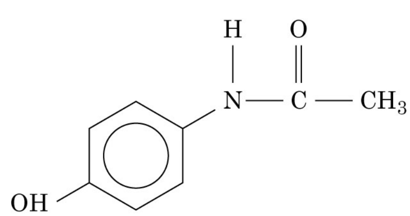
7.32 **a)** The two compounds are 2,4-dichlorophenol and glycolic acid (hydroxyacetic acid).





b) If its two chlorine atoms are replaced by hydrogen atoms, the compound with the structure on the left becomes phenol. The compound on the right becomes ethanol if its —COOH group is changed to a —CH_3 group.

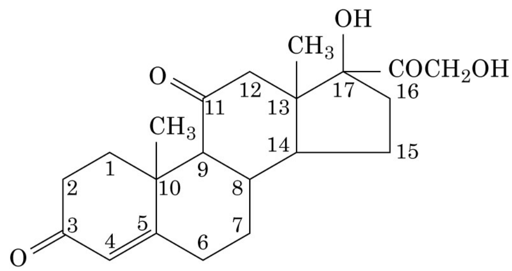
7.34 **a)** Acetaminophen, the active ingredient in Tylenol, has the molecular formula $C_8H_9NO_2$. Chemical names include N-(4-hydroxyphenyl)acetamide and N-acetyl-*p*-aminophenol. The structure is



b)

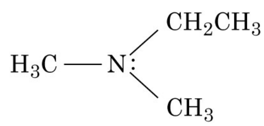
$$n = 0.500 \text{ g } C_8H_9NO_2 \times \left(\frac{1 \text{ mol } C_8H_9NO_2}{151.16 \text{ g}}\right) = 3.31\times10^{-3} \text{ mol } C_8H_9NO_2$$

7.36 The structure and numbering of the atoms in the steroid cortisone ($C_{21}H_{28}O_5$) are



To make testosterone ($C_{19}H_{28}O_2$), the carbonyl group C═O at C-11 in cortisone is reduced to —CH_2—, and the —$COCH_2OH$ side-group at C-17 is replaced by —H. Changes that appear minor alter physiological function greatly.

7.38 The compound must be a tertiary amine



No other structural formulas are possible.

7.40 **a)** Five candidate structures are proposed for benzene: 1,3,5-cyclohexatriene (i), conjugated cyclohexatriene (ii), 1-methylene-2,4-cyclopentadiene (iii), 2,4-hexadiyne (iv), and 1,5-hexadiene-3-yne (v). Structures (i), (ii), and (iv) can form only one C_6H_5Cl. They are consistent with the observation of only one isomer of C_6H_5Cl The other two structures accommodate Cl in place of H in at least two distinct locations.

b) Only structure (ii) gives exactly three isomers of formula $C_6H_4Cl_2$ (1,2-, 1,3-, and 1,4-dichlorobenzene). Structures (i), (iii), and (v) give more than three isomers, and structure (iv) gives only two isomers.

7.42 Make an alcohol that is enriched in an isotope of oxygen, such as $R(^{18}O)H$. Prepare the ester and determine how much, if any, of the heavier isotope is incorporated in it. The experiment has been performed. The result is that almost all of the labeled oxygen is incorporated in the ester. The oxygen in an ester comes almost entirely from the alcohol rather than the carboxylic acid.

7.44 **a)** Dehydration reactions extract H_2O from organic compounds and leave different organic substances behind, depending on conditions

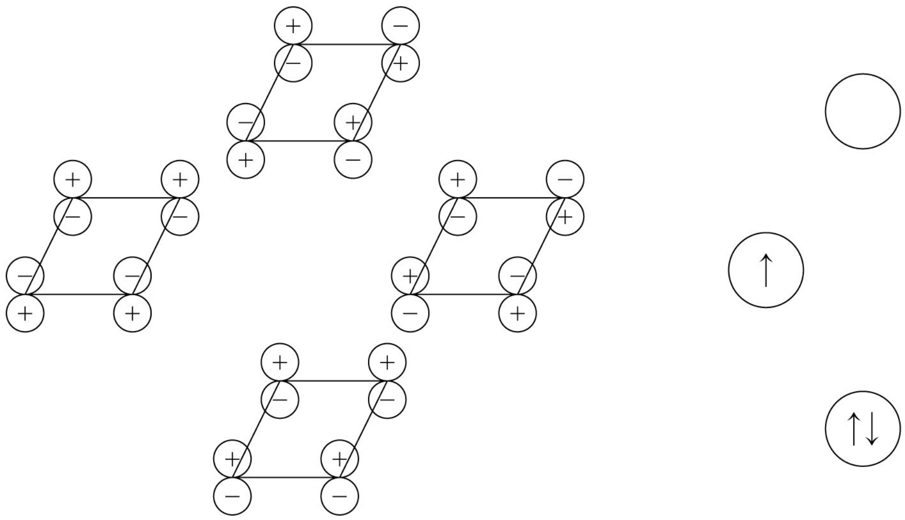
$$CH_3CH_2OH \rightarrow CH_2 = CH_2 + H_2O \qquad \text{over alumina, } 400°C$$

$$2CH_3CH_2OH \rightarrow CH_3CH_2\text{—O—}CH_2CH_3 + H_2O \qquad \text{over alumina, } 230°C$$

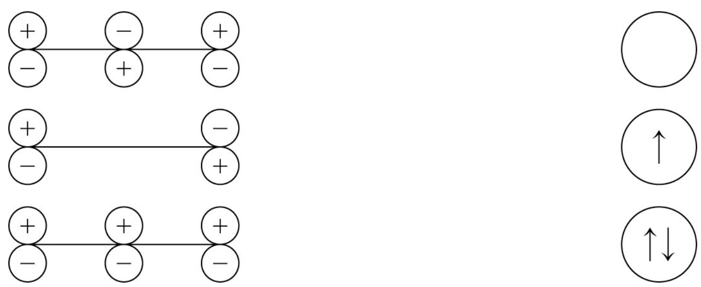
b) At temperatures well above 400°C, all of the oxygen stays in the compound and the reaction is a dehydrogenation

$$CH_3CH_2OH \rightarrow CH_3C(H){-}O + H_2$$

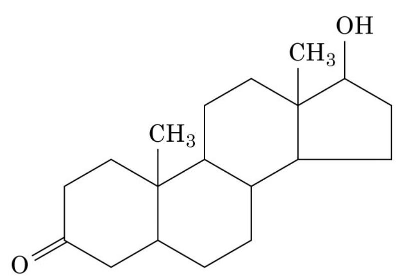
7.46 **a)** Cyclobutadiene is paramagnetic. Its four 2*p* orbitals overlap to give the π MO system indicated in the following. As shown, two of these π orbitals have identical energy on the basis of their symmetry.



b) The linear allyl radical is paramagnetic



7.48 **a)** The structure of stanolone is



b) The molecular formula of stanolone is $C_{19}H_{30}O_2$.

7.50 The more widely delocalized π electrons in naphthalene have longer characteristic wavelengths than the π electrons in benzene. The wavelength of maximum absorption of light will accordingly be shifted to a wavelength longer than 255 nm.

Chapter 8

Bonding in Transition Metals and Coordination Complexes

8.2 $TiCl_4$ and $TiBr_4$ are both covalent compounds. They consist in the solid phase of strongly bonded molecules linked together in long-range order by weaker intermolecular attractions. These weak intermolecular attractions are somewhat stronger in $TiBr_4$ than in $TiCl_4$ because $TiBr_4$ has more electrons. TiF_4 has a far higher melting point than either $TiCl_4$ or $TiBr_4$ because its bonds have far more ionic character, causing the distinction between intermolecular and intramolecular attractions to disappear. The attractions maintaining the solid in TiF_4 are thus stronger.

8.4 The chemical formula of vanadium(III) oxide is V_2O_3. This compound should be more basic than the higher oxide V_2O_5 (which appears in problem **8.3**).

$$V_2O_3(s) + 6\ H_3O^+(aq) \rightarrow 2\ V^{3+}(aq) + 9\ H_2O(l)$$

8.6 The balanced equation is $6\ COO(s) + O_2(g) \rightarrow 2\ CO_3O_4(s)$. The average oxidation state of CO in CO_3O_4 is $\frac{8}{3}$. This corresponds to two CO^{3+} ions and one CO^{2+} ion.

8.8 The oxidation state of Nb in Nb_2O_5 is +5; the oxidation state of Mo in MoS_2 is +4; the oxidation state of Ru in $RuCl_3$ is +3; the oxidation state of Rh in RhO_2 is +4; the oxidation state of Pd in PdF_2 is +2; and the oxidation state of Ag in Ag_2O is +1.

8.10 The hydroxide ion is a hard base but it does not have the high charge density of anions such as F^- and O^{2-} required to stabilize metals in high oxidation states; the charge density is suitable for stabilizing metals in intermediate oxidation states.

8.12 Chloride (though not listed in Table 8.2) can be considered to be a borderline hard acid by comparison with its neighbors fluoride and bromide. Cu^{2+} is a soft acid that would prefer to be paired with the soft base S^{2-} so the reaction is likely to proceed as written.

8.14 The oxidation state of Cr in CrO_2 is +4 whereas it is +3 in Cr_2O_3. Metals in higher oxidation states tend to form more covalent bonds whereas those in lower oxidation states tend to form more ionic bonds. These considerations suggest that the melting point of Cr_2O_3 should be higher than that of CrO_2.

8.16 The glycinate ion ($H_2N—CH_2—COO^-$) has two donor sites. They are the nitrogen atom, which has one lone pair of electrons, and the carboxylate oxygen atom, which has three lone pairs. The ligand can bind to a metal ion by donating electron pairs from either of these sites or both.

8.18 The oxidation state of Mn in $Mn_2(CO)_{10}$ is zero; the oxidation state of Re in $[Re_3Br_{12}]^{3-}$ is +3; the oxidation state of the Fe in $[Fe(H_2O)_4(OH)_2]^+$ is +3; the oxidation state of the Co in $[Co(NH_3)_4Cl_2]^+$ is +3.

8.20 **a)** $Ag_4[Fe(CN)_6]$ **b)** $K_2[Co(NCS)_4]$ **c)** $Na_3[VF_6]$ **d)** $K_3[Cr(C_2O_4)_3]$

8.22 **a)** tetraaquadihydroxonickel(II) **b)** chloroiodomercury(II)

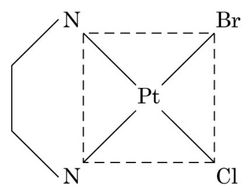
c) potassium hexacyanoosmate(II) **d)** bromochlorobis(ethylenediamine)iron(III) chloride

8.24 Conductivity increases in the order

$$\left[Fe(NH_3)_3Cl_3\right] < \left[Cr(NH_3)_4Cl_2\right]Cl < BaCl_2 < K_4\left[Fe(CN)_6\right]$$

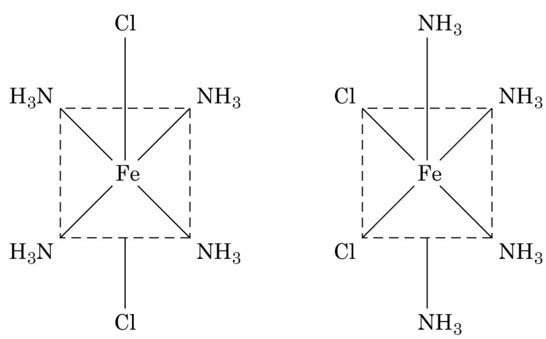
The number of ions released in water per molecule of solute increase in this sequence from 0 to 2 to 3 to 5.

8.26 **a)** The square-planar complex bromochloro (ethylenediamine) platinum(II) has only one isomer (the $NH_2CH_2CH_2NH_2$ ligand cannot span *trans* positions). The structure is



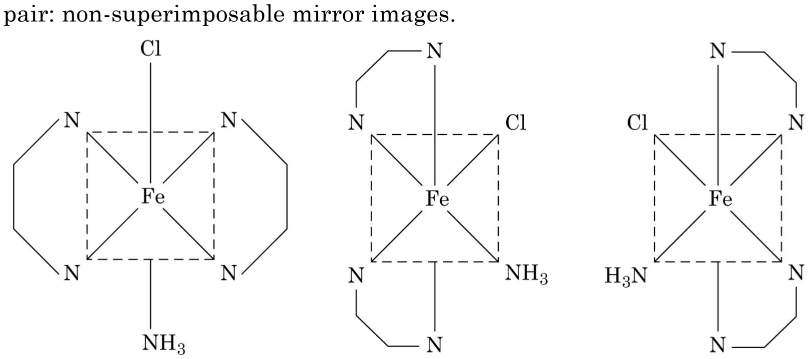
b) The complex ion has *trans* and *cis* isomers just like those of text Figure 8.11 except with a central iron(III) ion.

trans



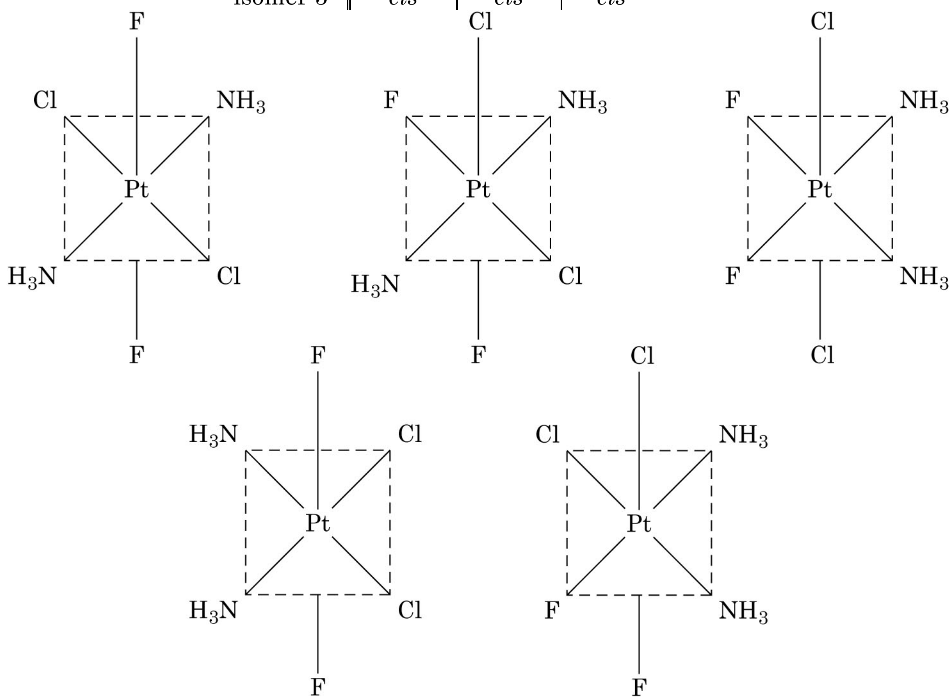
cis

c) The amminechlorobis (ethylenediamine) iron(III) ion, a +2 ion, has a *trans* isomer (at the left in the following) and two *cis* isomers. The *cis* isomers (center and right in the following) are an enantiomeric pair: non-superimposable mirror images.



8.28 There are two each of the three ligands NH_3, Cl^-, and F^-. The members of each pair may be either *cis* or *trans* about the central Pt(IV) in octahedral coordination. This would seem to mean that there are eight isomers corresponding to the eight possible triple combinations of *cis* and *trans (cis-cis-cis, cis-cis-trans, cis-trans-cis,* and so forth). But placing two pairs of like ligands *trans* forces the third pair also to be *trans*. This eliminates *cis-trans-trans, trans-cis-trans, and trans-trans-cis* from the list of eight. Only these five *cis-trans* isomers are possible:

	NH_3	Cl	F
isomer 1	*trans*	*trans*	*trans*
isomer 2	*trans*	*cis*	*cis*
isomer 3	*cis*	*trans*	*cis*
isomer 4	*cis*	*cis*	*trans*
isomer 5	*cis*	*cis*	*cis*



Each of these isomers is now scrutinized to see if it is superimposable on its mirror image. Any isomer that has even one *trans* disposition of ligands has a plane of symmetry and *is* superimposable on its mirror image. This applies to four of the above five cases. The *cis-cis-cis* geometry (bottom right) is *not* superimposable on its mirror image and exists as a pair of enantiomers.

8.30 See table 8.5.

a) The Cr^{2+} ion is a d^4 case. In a strong octahedral field it has the ground-state configuration t_{2g}^4, which means it has two unpaired electrons; in a weak octahedral field the configuration is $t_{2g}^3 e_g^1$ all four electrons are unpaired.

b) The V^{3+} ion is a d^2 case. It has two unpaired electrons (electron configuration t_{2g}^2) in both a strong and a weak octahedral field.

c) The Ni^{2+} ion is a d^8 case. It has the configuration $t_{2g}^6 e_g^2$ for two unpaired electrons in both a strong and a weak octahedral field.

d) The Pt^{4+} ion is a d^6 case. It has four unpaired electrons in a weak octahedral field $\left(t_{2g}^4 e_g^2\right)$f and no unpaired electrons $\left(t_{2g}^6\right)$ in a strong octahedral field.

e) The Co^{2+} ion is a d^7 case. It has three unpaired electrons in a weak octahedral field $\left(t_{2g}^5 e_g^2\right)$ and one unpaired electron $\left(t_{2g}^6 e_g^1\right)$in a strong octahedral field.

8.32 The Mn(III) ion in these two complexes has four *d electrons*. When coordinated by Cl^- in the $[MnCl_6]^{3-}$ ion, the result is a high-spin complex-all four electrons are unpaired. With a stronger-field ligand in the $[Mn(CN_6)]^{3-}$ there are no electrons in the higher-energy e_g levels. Putting four electrons into the t_{2g} level requires pairing two. The other two are unpaired. In the first case, the CFSE is $-\frac{3}{5}\Delta_o$; in the second it is $-\frac{8}{5}\Delta_o$.

8.34 The problem concerns the standard reduction potentials of Mn^{3+}(aq), Fe^{3+}(aq) and Co^{3+}(aq) to the corresponding 2+ ions. All six of the ions are octahedrally coordinated by H_2O

molecules in acidic aqueous solution. The metals in the 3+ ions are d^4, d^5, and d^6 species; the metals in the 2+ ions are d^5, d^6 and d^7 species, respectively. These hexaaqua complexes are all high-spin complexes because water is a weak-field ligand. The reduction potential of $Fe^{3+}(aq)$ is less than the reduction potential of its neighbors in the periodic table, which means that it is *harder* to reduce to the +2 state than the neighbors. The $Fe^{3+}(aq)$ ion has the high-spin $t_{2g}^3 e_g^2$ configuration. This is a relatively stable electron configuration relative to configurations with four or six d-electrons (note that both the e_g and the t_{2g} levels of Fe^{3+} are half-filled). As a consequence, the $Fe^{3+}(aq)$ ion resists reduction better.

8.36 Seeing a black solution means that the $[PtI_6]^{2-}$ ion absorbs all across the visible spectrum.

8.38 A solution of hexaaquanickel(II) ion is green because it absorbs the complementary color of green, which is red. Use text Figure 4.3 to estimate the wavelength of the absorption in the red as 700 nm. The corresponding energy is

$$E = \frac{hc}{\lambda} = \frac{\left(6.626\times10^{-34}\text{ J s}\right)\left(3.00\times10^{8}\text{ m s}^{-1}\right)}{700\times10^{-9}\text{ m}} = 2.8\times10^{-19}\text{ J}$$

The absorption occurs with the excitation of an electron from a t_{2g} to an e_g level so this energy is Δ_o. Multiplying Δ_o by Avogadro's number puts it on a molar basis. It is about 170 KJ mol^{-1}.

8.40 The CFSE for this d^8 complex is $-\frac{6}{5}\Delta_o$, or about -200 KJ mol^{-1}.

8.42 **a)** The complement of yellow is violet; the hexaamminecobalt(III) ion absorbs in the violet.
b) Estimate the wavelength from knowledge of the wavelength of the complement of the observed color. It is probably near 410 nm as a maximum (see text Figure 4.3).

8.44 **a)** The complex $\left[Mn(H_2O)_6\right]^{2+}$ results from the dissolution of $Mn\left(NO_3\right)_2$ in water. It is a high-spin d^5 complex. The excitation of an electron requires the reversal of a spin; such processes are close to being strictly forbidden. Their rarity makes the color of the ion faint. The $[Mn(CN)_6]^{4-}$ ion on the other hand is a low-spin complex. The $t_{2g} \rightarrow e_g$ transitions are not spin-forbidden and are more intense.

b) $Zn\left(NO_3\right)_2$, $CdSO_4$ and $AgClO_3$ should be colorless in aqueous solution, because of the full occupancy of the d orbitals of the metal ion when coordinated by the solvent.

8.46 The geometry of $[NiCl_4]^{2-}$ is predicted to be tetrahedral because Cl^- is a weak field ligand and the corresponding Ni – Cl bonds are relatively ionic. One of the t_{2g} orbitals is doubly occupied and a single electron occupies each of the other t_{2g} orbitals; the compound is paramagnetic. The geometry of $[Ni(CN)_4]^{2-}$ is predicted to be square planar because CN^- is a π- acceptor, strong field ligand. Each of the four lowest energy orbitals is doubly occupied and the compound is diamagnetic.

8.48 Text Appendix E (but not text Table 8.1) gives the standard reduction potentials of the three metal ions to metallic form. The standard reduction potential of the $Cu^{2+}(aq)$ is $+0.34$ V, which is much larger than that of either $Ni^{2+}(aq)$ ion (–0.23 V) or $Zn^{2+}(aq)$ ion (–0.76 V). Let M stand for the metal (Ni, Cu, or Zn). The four steps in the left-most column of following table add up to an overall process taking solid metal into aqueous solution:

		Ni	Cu	Zn	
$M(s) \rightarrow M(g)$	ΔH	430	338	131	kJ mol^{-1}
$M(g) \rightarrow M^+(g) + e^-$	ΔU	737	745	906	
$M^+(g) \rightarrow M^{2+}(g) + e^-$	ΔU	1753	1958	1733	
$M^{2+}(g) \rightarrow M^{2+}(aq)$	ΔH	-2985	-2989	-2937	
$M(s) \rightarrow M^{2+}(aq) + 2\,e^-$		-65	52	-167	

The numerical data in the first line in the table come from text Appendix D; other data come from text Table 8.1. The bottom line gives the sum of the preceding entries. The table mixes internal energies *(U*'s*)* and enthalpies *(H*'s), but the difference between these two quantities is small for these reactions. The endothermic result (+52 kJ mol^{-1}) for Cu(*s*) compared to the exothermic (negative) results for the Ni(*s*) and Zn(*s*) indicates the greater stability of Cu(*s*) in this reaction or, equivalently, the greater tendency of $Cu^{2+}(aq)$ to be reduced to Cu(*s*).

8.50 The reaction is

$$2\left[Cr(en)_2(NCS)_2\right]SCN(s) \rightarrow \left[Cr(en)_2(NCS)_2\right]\left[Cr(en)(NCS)_4\right](s) + en(g)$$

The oxidation number of the chromium does not change from +3 in this reaction. Rather, two NCS^- anions replace an ethylenediamine in the coordination sphere of one of the complexes.

8.52 $2\,(NH_4)_2\left[Ir(H_2O)Cl_5\right] \rightarrow NH_3(g) + 2\,H_2O(g) + HCl(g) + (NH_4)_3\left[Ir_2Cl_9\right]$. The name of the starting material is ammonium aquapentachloroiridate(III).

8.54 **a)** $[Fe(H_2O)_5Cl]CO_3$ is most likely to have the same electrical conductivity per mole as $MgSO_4$, which is also a 2 to 2 ionic compound.
b) $[Mn(H_2O)_6]Cl_3$ matches best to $GaCl_3$, which also has Cl^- as the anion, but also matches to Na_3PO_4.
c) $[Zn(H_2O)_3(OH)]Cl$ matches best to NaCl.
d) $[Fe(NH_3)_6]_2(CO_3)_3$ matches best to $Fe_2(SO_4)_3$.
e) $[Cr(NH_3)_3Br_3]$ matches best to HCN; both are nonelectrolytes.
f) $K_3[$**Fe**$(CN)_6]$ matches well to both Na_3PO_4 and $GaCl_3$.

8.56 A planar hexagonal structure for $[Co(NH_3)_4Cl_2]^+$ would have three isomers: one with the two Cl's next to each other, one with the two Cl's separated by one NH_3, and one with the two Cl's separated by two NH_3's around the hexagonal ring. A trigonal prismatic structure would have three isomers as well: one with both Cl's on the same triangular end of the prism, one with the two Cl's on opposite triangular ends and lying on the same edge, and one with the two Cl's on opposite ends and lying on different edges. The last of these would be chiral.

8.58 The compound has an odd number of valence electrons and will be paramagnetic.

8.60 In a crystal field of octahedral symmetry all three *p* orbitals have the same energy. There is no **splitting**. Electrons in the *p* orbitals have their greatest probability density along a coordinate axis and differ among themselves only in which axis. The axes are indistinguishable in the octahedral case; each has one ligand on each end. A square-planar field is derived from an octahedral field by removal of ligands from one axis, say, the *z*. If so, the p_z orbital would be split to lower energy (since it would not encounter ligands directly) while the p_y and p_x orbitals would remain unsplit.

8.62 Mn^{2+} is not a strong reducing agent because it appears high up on the right side of the table in Appendix E (it is difficult to *oxidize* Mn^{2+} to Mn^{3+} because the *reduction* potential of the reverse reaction, 1.51 V, is so high).
Mn^{2+} is not a strong oxidizing agent because it appears far down on the left side of Appendix E (it is difficult to reduce it because its reduction potential to Mn(*s*), -1.029 V, is so negative). Conclusion: $Mn^{2+}(aq)$ is unusually stable compared to other metal ions.

8.64 The $Mn^{2+}(aq)$ ion, which is actually the $[Mn(H_2O)_6]^{2+}$ ion, is a high-spin complex involving the weak-field ligand H_2O. Nothing in problem **8.51** gives any insight as to whether $Mn^{2+}(aq)$ is more easily oxidized or reduced. The standard reduction potentials in text Appendix D indicate that $Mn^{2+}(aq)$ ion is quite stable relative to disproportionation to $Mn^{3+}(aq)$ ion and Mn(*s*).

8.66 **a)** The compound $(NH_4)_2[Fe(H_2O)F_5]$ has an odd number of valence electrons and is paramagnetic regardless on the strength of the ligands. Because the ligands are weak-field ligands, the octahedral field is weak and the five *d* electrons of the Fe(III) should remain unpaired. This makes the compound paramagnetic to the extent of five unpaired electrons.

b) The anion is a high-spin d^5 complex like $[Fe(H_2O)_6]^{3+}$ so the complex is probably a pale violet. Note that the cation (the ammonium ion) is colorless.

c) The electron configuration of the *d* electrons of the iron is $t_{2g}^3 e_g^2$.

d) The compound is named ammonium aquapentafluoroferrate(III).

8.68 The C—O bond length should be increased in $Ni(CO)_4$, relative to the free molecule, because of π-back-bonding. This has the effect of delocalizing the $3d^8$ electrons of Ni over the π^* orbital of each CO, thereby lowering its bond energy, increasing its bond length, and lowering its vibrational frequency.

8.70 The compound $[V(N_2)_6]$ should be octahedral with the six ligands arranged around the central V atom. The compound has an odd number of valence electrons and is paramagnetic. It is isoelectronic with $[V(CO)_6]$.

8.72 The $C_5H_5^-$ ion (cyclopentadienyl ion) is stabilized by resonance, like benzene. After tungsten has donated its two 6*s* electrons to C_5H_5 molecules to make a pair of such ions, it retains its four 5*d* electrons (d^4). Tantalum, which is just to the left of tungsten in the periodic chart, retains its three 5*d* electrons (d^3) after a similar transaction. Tungsten then shares two electrons with two H atoms to form single bonds. Afterward it still has two *d* electrons left to attract an approaching H^+ ion. This means that $WH_2(C_5H_5)_2$ serves effectively as a base. In contrast, tantalum must share all three *d* electrons with H atoms to make $WH_3(C_5H_5)_2$. The compound has little valence electron density to offer an incoming H^+ ion.

8.74 The reaction is

$$2\ \mathrm{Sc}(s) + 6\ \mathrm{H_3O^+}(aq) \rightarrow 2\ \mathrm{Sc^{3+}}(aq) + 6\ \mathrm{H_2O}(l) + 3\ \mathrm{H_2}(g)$$

$$n_{\mathrm{H_2}} = \left(\frac{4.53\ \mathrm{g\ Sc}}{44.956\ \mathrm{g\ mol^{-1}}}\right) \times \left(\frac{3\ \mathrm{mol\ H_2}}{2\ \mathrm{mol\ Sc}}\right) = 0.151\ \mathrm{mol\ H_2}$$

Assuming 1 atm pressure and 25°C,

$$V_{\mathrm{H_2}} = \frac{nRT}{P} = \frac{(0.151\ \mathrm{mol})(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})(298\ \mathrm{K})}{1.00\ \mathrm{atm}} = 3.70\ \mathrm{L}$$

8.76 The chemical amount and mass of CO released by the heating are

$$n_{\mathrm{CO}} = \frac{PV}{RT} = \frac{(2.00\ \mathrm{atm})(1.18\ \mathrm{L})}{(0.08206\ \mathrm{L\ atm\ mol^{-1}K^{-1}})(298\ \mathrm{K})} = 0.09651\ \mathrm{mol}$$

$$m_{\mathrm{CO}} = (0.09651\ \mathrm{mol\ CO})(28.01\ \mathrm{g\ mol^{-1}}) = 2.70\ \mathrm{g}$$

so the mass and number of moles of the osmium in the original sample were

$$m_{\mathrm{Os}} = 6.79 - 2.70 = 4.09\ \mathrm{g} \quad \text{and} \quad n_{\mathrm{Os}} = \frac{4.09\ \mathrm{g\ Os}}{190.2\ \mathrm{g\ mol^{-1}}} = 0.02150\ \mathrm{mol}$$

The ratio of the chemical amount of CO to that of Os is $\frac{0.09651\ \mathrm{mol}}{0.02150\ \mathrm{mol}} = 4.489 \approx 4.5 = \frac{9}{2}$

The probable empirical formula is $Os_2(CO)_9$. This compound might have a single bridging CO ligand, with four other CO molecules attached separately to each Os atom.

Chapter 9

The Gaseous State

9.2 Look for molecules of known gases (such as carbon dioxide or ammonia or hydrogen sulfide) that might be split off from larger molecules. The balanced equation is

$$NH_4CO_2NH_2(s) \rightarrow 2\ NH_3(g) + CO_2(g)$$

9.4 The acidification of aqueous solutions of KCN causes the evolution of poisonous HCN(g) according to the equation: $CN^-(aq) + H^+(aq) \rightarrow HCN(g)$.

9.6 **a)** Assume that the levels of the mercury in the two arms of the mercury-containing gauge are equal when the gauge is attached to a vessel that contains no gas. Then

$$P = \rho g h = (13.60 \times 10^3 \text{ kg m}^{-3})(9.806 \text{ m s}^{-2})(0.0950 \text{ m}) = 1.267 \times 10^4 \text{ Pa} = 0.125 \text{ atm}$$

b) Assume the levels of the DBP oil in the two arms of the oil-containing gauge are equal when the gauge is attached to a vessel that contains no gas. Then

$$\rho_{Hg}\ g\ h_{Hg} = \rho_{DBP}\ g\ h_{DBP}$$

$$h_{DBP} = \frac{\rho_{Hg}}{\rho_{DBP}} h_{Hg} = \left(\frac{13.60 \text{ g cm}^{-3}}{1.045 \text{ g cm}^{-3}}\right)(9.50 \text{ cm}) = 124 \text{ cm} = 1.24 \text{ m}$$

9.8 A 76 cm column of mercury exerts the same pressure at its base that the atmosphere does on the surface of 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 almost perfectly 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 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 (in problem **9.7**), the atmosphere is nowhere near uniform in density. The decrease in density of the atmosphere with altitude means that it is much thicker than 8 km.

9.10 Use the information in Table 9.2 in the text

$$P = 5\times10^{-10}\ \text{torr}\times\left(\frac{1\ \text{atm}}{760\ \text{torr}}\right) = 7\times10^{-13}\ \text{atm}$$

$$= 5\times10^{-10}\ \text{torr}\times\left(\frac{1\ \text{atm}}{760\ \text{torr}}\right)\times\left(\frac{1.01325\times10^{5}\ \text{Pa}}{1\ \text{atm}}\right) = 7\times10^{-8}\ \text{Pa}$$

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

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

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

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

Convert the Celsius temperatures given in the problem to absolute temperatures and substitute

$$V_2 = \left(\frac{(273.15+40.0)\ \text{K}}{(273.15+20.0)\ \text{K}}\right)(4.00\ \text{L}) = 4.27\ \text{L}$$

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

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

Convert the temperature to the Kelvin scale and substitute the volumes

$$T_2 = \left(\frac{5.26\ \text{L}}{5.40\ \text{L}}\right)\times299.65\ \text{K} = 291.88\ \text{K}$$

Converting back to the Celsius scale gives 18.7°C.

9.18 Use Charles's law, as in problem **9.16**, but now to get a volume

$$V_2 = \left(\frac{T_2}{T_1}\right)V_1 = \left(\frac{(273.15+230)\ \text{K}}{(273.15+20)\ \text{K}}\right)\times3.41\ \text{L} = 5.85\ \text{L}$$

9.20 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 × 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.

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{which gives} \quad V_2 = \left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)V_1$$

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

9.24 **a)** Calculate the number of moles of O_2 corresponding to 0.30 kg of O_2. It is 9.375 mol O_2. Assume that O_2 is an ideal gas. If so, its pressure in the scuba tank is

$$P = \frac{nRT}{V} = \frac{9.375 \text{ mol } \left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)278.15 \text{ K}}{2.32 \text{ L}} = 92 \text{ atm} = 1.4\times10^{3} \text{ psi}$$

b)

$$V_2 = \left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)V_1 = \left(\frac{92 \text{ atm}}{0.98 \text{ atm}}\right)\left(\frac{303 \text{ k}}{278 \text{ k}}\right)\left(2.32 \text{ L}\right) = 2.4\times10^{2} \text{ L}$$

9.26 **a)** $2\ \text{Al}(s) + 6\ \text{HCl}(aq) \rightarrow 3\ \text{H}_2(g) + 2\ \text{AlCl}_3(aq)$.

b) Assume that the hydrogen behaves ideally and use the ideal-gas equation

$$n_{\text{H}_2} = \frac{PV}{RT} = \frac{\left(0.750 \text{ L}\right)\left(10.0 \text{ atm}\right)}{\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(273.15+30.0\right)\text{K}} = 0.3015 \text{ mol}$$

$$m_{\text{A}_1} = 0.3015 \text{ mol H}_2\left(\frac{2 \text{ mol Al}}{3 \text{ mol H}_2}\right)\left(\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}\right) = 5.42 \text{ g Al}$$

9.28 **a)** $\text{Fe}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{H}_2(g) + \text{FeSO}_4(aq)$.

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 $V = \frac{4}{3}\pi r^3$ 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).

9.30 Use the ideal-gas law to get the amount of Cl_2. Then use the 1 : 1 stoichiometric ratio of Cl_2 to MnO_2 from the balanced equation

$$n_{\text{Cl}_2} = \frac{PV}{RT} = \frac{\left(0.953 \text{ atm}\right)\left(5.32 \text{ L}\right)}{\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(306.15 \text{ K}\right)} = 0.2018 \text{ mol}$$

$$m_{\text{MnO}_2} = 0.2018 \text{ mol Cl}_2\left(\frac{1 \text{ mol MnO}_2}{1 \text{ mol Cl}_2}\right)\left(\frac{86.937 \text{ g MnO}_2}{1 \text{ mol MnO}_2}\right) = 17.5 \text{ g MnO}_2$$

9.32 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

$$n_{O_3} = 4.69 \text{ g KO}_3\left(\frac{1 \text{ mol KO}_3}{87.10 \text{ g KO}_3}\right)\left(\frac{5 \text{ mol O}_3}{2 \text{ mol KO}_3}\right) = 0.1346 \text{ mol O}_3$$

From the ideal gas law,

$$V_{O_3} = \frac{n_{O_3}RT}{P} = \frac{(0.1346 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(258.15 \text{ K})}{0.134 \text{ atm}} = 21.3 \text{ L}$$

9.34 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 its mole fraction multiplied by the total pressure, as long as the mixture behaves according to Dalton's law. $P_{NH_3} = 20$ atm.

9.36 Assume ideal-gas behavior, despite that rather high total pressure. For mixtures of ideal gases, mole fractions are the same as fractions by volume, so the mole fraction of N_2 at the surface of Venus is 0.035. The partial pressure of N_2 is 3.2 atm, the mole fraction multiplied by the total pressure.

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

9.40 **a)** Use the partial pressure of O_2(g) in the ideal-gas equation

$$n_{O_2} = \frac{P_{O_2}V}{RT} = \frac{(0.200 \text{ atm})(1.500 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(313.15 \text{ K})} = 1.167\times10^{-2} \text{ mol O}_2$$

$$N_{O_2} = (1.167\times10^{-2} \text{ mol})(6.022\times10^{23} \text{ mol}^{-1}) = 7.03\times10^{21} \text{ molecules}$$

b) Oxygen is the limiting reactant. $2\text{ H}_2(g) + \text{O}_2(g) \rightarrow 2\text{ H}_2\text{O}(l)$

$$n_{H_2O} = \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2}\right)(1.167\times10^{-2}\text{mol O}_2) = 2.335\times10^{-2}\text{mol H}_2\text{O}$$

$$m_{H_2O} = (2.335\times10^{-2}\text{mol H}_2\text{O})(18.02 \text{ g mol}^{-1}) = 0.421 \text{ g H}_2\text{O}$$

9.42 Use text equation 9.16

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

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

9.44 Substitute the molar masses of helium, argon, and xenon atoms in kg mol^{-1} successively into text equation 9.16

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

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.

9.46 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%.

9.48 Solve the van der Waals equation for pressure and substitute:

$$\begin{aligned} P &= \frac{nRT}{V-nb} - a\left(\frac{n^2}{V^2}\right) \\ &= \frac{\left(140\times10^6/18.0153\right)\text{mol}\left(0.08206\text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(813.15\text{ K}\right)}{\left(2500\times10^3\text{ L}\right)-\left(140\times10^6/18.0153\right)\text{ mol}\left(0.03049\text{ L mol}^{-1}\right)} \\ &\quad -\left(5.464\text{ atm L}^2\text{ mol}^{-2}\right)\left(\frac{\left(140\times10^6/18.0153\right)^2\left(\text{mol}\right)^2}{\left(2500\times10^3\text{ L}\right)^2}\right) \\ &= 176\text{ atm} = 2590\text{ psi} \end{aligned}$$

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

a) Using the ideal gas equation

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

b) Using the van der Waals equation

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

The T computed using the VDW equation exceeds the ideal-gas T. The numerator in the the fraction in the last equation is increased by a and decreased by b. Hence a in more important than b in this case, that is, attractive forces are more important than excluded volume.

9.52

$$n_{H_2} = \frac{(0.001 \text{ atm})(0.200 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(298 \text{ K})} = 8.18\times10^{-6} \text{ mol}$$

$$Z_w = \text{rate of loss} = \frac{(8.18\times10^{-6}\text{mol})(6.022\times10^{23} \text{ mol}^{-1})}{3600 \text{ s}} = 1.37\times10^{15} \text{ s}^{-1}$$

$$= \frac{1}{4}\frac{N}{V}\bar{u}A = \frac{1}{4}\frac{N_A P}{RT}\bar{u}A$$

$$\bar{u}_{H_2} = \sqrt{\frac{8RT}{p\text{M}}} = \sqrt{\frac{8(8.3145 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{p(2.016\times10^{-3}\text{kg mol}^{-1})}} = 1770 \text{ m s}^{-1}$$

$$A = \frac{4RT\ Z_w}{N_A P \bar{u}}$$

$$= \frac{4(8.3145 \text{ Jmol}^{-1} \text{ K}^{-1})(298 \text{ K})(1.37\times10^{15}\text{s}^{-1})}{(6.022\times10^{23}\text{mol}^{-1})(0.990 \text{ atm})(101325 \text{ Pa atm}^{-1})(1770 \text{ m s}^{-1})} = 1.27\times10^{-13} \text{ m}^2$$

$$r = \sqrt{\frac{A}{p}} = \sqrt{\frac{1.27\times10^{-13}\text{m}^2}{p}} = 2\times10^{-7}\text{m}^2$$

9.54 Apply Graham's law of effusion. The initial ratio of the rates of effusion is

$$\frac{\text{rate}_{F_2}}{\text{rate}_{BrF_5}} = \sqrt{\frac{\mathcal{M}_{BrF_5}}{\mathcal{M}_{F_2}}} = \sqrt{\frac{174.896}{37.997}} = 2.145$$

As effusion continues the remaining mixture becomes enriched in BrF_5 and this ratio drops.

9.56

$$\frac{\text{rate}_{He}}{\text{rate}_{H_2}} = 3.00 = \frac{N_{He}}{N_{H_2}}\sqrt{\frac{m_{H_2}}{m_{He}}} \quad \text{from which} \quad \frac{N_{He}}{N_{H_2}} = 3.00\sqrt{\frac{m_{He}}{m_{H_2}}} = 3.00\sqrt{1.986} = 4.227$$

$$X_{H_2} = \frac{N_{H_2}}{N_{H_2} + N_{He}} = \frac{N_{H_2}}{N_{H_2} + 4.227N_{H_2}} = 0.191$$

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

$$\left(\frac{N_{H_2}}{N_{He}}\right)_n = \left(\frac{N_{H_2}}{N_{He}}\right)_0 (1.409)^n = \frac{1}{4.227}(1.409)^n$$

For 99.9% purity, $N_{H_2}/N_{He} = (99.9/0.1) = 999$. Therefore

$$999 = \frac{1}{4.227}(1.409)^n \quad \text{from which} \quad 4223 = (1.403)^n$$

Solving gives n = 24.7. Thus 25 stages are required.

9.58 Get the mean free path λ in terms of the pressure and temperature using $N/V = PN_4/RT$

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

Solve for P and substitute, letting $\lambda = d$, the diameter of the Kr atom

$$P = \frac{RT}{\sqrt{2}\pi d^2 \lambda N_A} = \frac{(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(300 \text{ K})}{\sqrt{2}\pi\left(3.16\times10^{-10}\text{m}\right)^2\left(3.16\times10^{-10}\text{ m}\right)\left(6.022\times10^{23}\text{mol}^{-1}\right)}$$
$$= 2.95\times10^{7} \text{ Pa} = 292 \text{ atm}$$

The diffusion constant D depends on λ and $\bar{u}$, the average speed of the Kr atoms

$$\bar{u} = \sqrt{8\ RT/\pi\mathcal{M}} = \sqrt{8\left(8.3145 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(300\text{K}\right)/\pi\left(0.083798 \text{ Kg mol}^{-1}\right)} = 275.3 \text{ m s}^{-1}$$

$$D = \frac{3\pi}{16}\lambda\bar{u} = 5.1\times10^{-8} \text{ m}^2 \text{ s}^{-1}$$

9.60 The outside pressure at the base of the basement walls is

$$P = \rho g h = \left(4.9\times10^{3} \text{ Kg m}^{-3}\right)\left(9.81 \text{ m s}^{-2}\right)\left(9.0 \text{ ft}\right)\left(0.3048 \text{ m ft}^{-1}\right)$$
$$= 1.32\times10^{5} \text{ kg m}^{-1} \text{ s}^{-2} = 1.32\times10^{5} \text{ Pa} = 1.3 \text{ atm}$$
$$= \left(1.3 \text{ atm}\right)\left(14.696 \text{ lb in}^{-2} \text{ atm}^{-1}\right) = 19 \text{ psi}$$

The inside pressure is 1 atm. The difference is 0.3 atm = 0.4 psi.

9.62 Set $V = 0$ in the equation in the problem and solve for t_F

$$-209.4 \text{ L} = \left(0.456 \text{ L°F}^{-1}\right)t_f \quad \text{from which} \quad t_f = -459\text{°F}$$

9.64 The density of an ideal gas is $\rho = \mathcal{M}P/RT$ where $\mathcal{M}$ is the molar mass. Write this equation for the initial state and again for the final state and divide the second by the first

$$\frac{\rho_2}{\rho_1} = \frac{P_2}{P_1}\frac{T_1}{T_2} \quad \text{from which} \quad \rho_2 = 1\left(\frac{323 \text{ K}}{423 \text{ K}}\right)\left(2.94 \text{ g L}^{-1}\right) = 2.24 \text{ g L}^{-1}$$

Solve the first equation for the molar mass and substitute

$$\mathcal{M} = \frac{\rho RT}{P} = \frac{2.94\text{g L}^{-1}\left(0.08206 \text{ L atm}^{-1} \text{ mol}^{-1} \text{ K}^{-1}\right)\left(323 \text{ K}\right)}{1.00 \text{ atm}} = 77.9 \text{ g mol}^{-1}$$

9.66 Assume that the air mixtures are all ideal gases. Their densities are given by $\rho = \mathcal{M}P/RT$ where $\mathcal{M}$ is the molar mass.

a) The hot dry air in July has a temperature of 35.0°C

$$\rho = \frac{\left(29.0 \text{ g mol}^{-1}\right)\left(1.00 \text{ atm}\right)}{\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(35.0 + 273.15\right)\text{K}} = 1.15 \text{ g L}^{-1}$$

b) The cool dry air in October has a temperature of 10.0°C

$$\rho = \frac{(29.0\ \text{g mol}^{-1})(1.00\ \text{atm})}{(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(10.0+273.15)\text{K}} = 1.25\ \text{g L}^{-1}$$

c) Saturating dry air with water vapor means adding a component to the mixture that has a molar mass less than that of N_2 or 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. 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.

9.68 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 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.

9.70 For every six molecules originally present, three are consumed, but two new molecules are generated for a total of five molecules. Thus n is multiplied by 5/6 with V and T constant. If the gases behave ideally, then P must be multiplied by 5/6

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

9.72 The balanced equation is $CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$. For every mole of CS_2(g) that reacts, the total number of moles drops by 1. Because the temperature and volume are the same before and after the reaction, the initial partial pressure of CS_2 must be equal in magnitude to the drop in total pressure, namely 3.00–2.40 = 0.60 atm.

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

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

9.74 **a)** The pressure is very low. Otherwise the frail walls made of light could not hold the gas.

$$P = \frac{nRT}{V} = \frac{500}{6.022\times10^{23}\ \text{mol}^{-1}}\frac{(8.3145\ \text{J K}^{-1}\text{mol}^{-1})(0.00024\ \text{K})}{1.0\times10^{-15}\text{m}^3} = 1.65\times10^{-9}\ \text{Pa}$$

b) Set up a ratio of the mean free path of the sodium atoms at room conditions (λ_2) to their mean free path in the optical trap (λ_1)

$$\frac{\lambda_2}{\lambda_1} = \frac{RT_2/(\sqrt{2}\pi d^2 N_A P_2)}{RT_1/(\sqrt{2}\pi d^2 N_A P_1)} = \frac{T_2P_1}{T_1P_2} = \frac{(298\ \text{K})(1.54\times10^{-9}\ \text{Pa})}{(0.00024\ \text{K})(1.013\times10^5\ \text{Pa})} = 2.0\times10^{-8}$$

Going from trap conditions to room conditions multiplies the mean free path by a factor of 2.0×10^{-8}. This reduces it from 3.9 m to about 8×10^{-8} m.

9.76 **a)** The average translational energy of molecules in an ideal gas is independent of their mass and thus of oxygen isotopic composition. For all species

$$\bar{E}_{200°C} = \tfrac{3}{2}RT = \tfrac{3}{2}\left(8.315 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(473 \text{ K}\right) = 5900 \text{ J mol}^{-1}$$
$$\bar{E}_{400°C} = \tfrac{3}{2}RT = \tfrac{3}{2}\left(8.315 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(673 \text{ K}\right) = 8390 \text{ J mol}^{-1}$$

b) The average molecular speed is given by $\bar{u} = \sqrt{8RT / \pi\mathcal{M}}$. The molar mass of the lightest dioxygen species, $^{16}O^{16}O$, is (approximately) 32.0 g mol^{-1}. The mass of the heaviest, $^{18}O^{18}O$, is 36.0 g mol^{-1}. The average speed of the 16–16 molecule at 200° C is

$$\bar{u}_{16-16} = \sqrt{\frac{8\left(8.315 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(473 \text{ K}\right)}{\pi\left(32.0\times10^{-3}\text{Kg mol}^{-1}\right)}} = 559 \text{ m s}^{-1}$$

A similar calculation gives $\bar{u}_{18-18} = 527 \text{ m s}^{-1}$. At 400°C, the corresponding average speeds 667 and 629 m s^{-1}.

9.78 **a)** From the right angle geometry in the figure, $r\cos\theta = \Delta l/2$ from which $\Delta l = 2r\cos\theta$.

b) A molecule is following the path marked by the lines with arrows on them. Its momentum is mu. The component of its momentum perpendicular to the wall at a point of collision is $mu \cos \theta$. After collision this component of momentum is $-mu\cos\theta$. The change in momentum during a collision is $\Delta p = -mu \cos\theta - \left(mu\cos\theta\right) = -2mu\cos\theta$. The change in momentum of the wall is equal and opposite: $\Delta p_{\text{wall}} = +2mu\cos\theta$.

c) Let the speed of the molecule equal u. The time Δt between collisions with the wall is $\Delta l/u$. The force on the wall by the molecule F_{wall} equal the momentum change per collision multiplied by the rate of collisions. The rate of collisions is $1/\Delta t$, so

$$F_{\text{wall}} = \Delta p_{\text{wall}}\left(\frac{1}{\Delta t}\right) = \Delta p_{\text{wall}}\left(\frac{u}{\Delta l}\right) = \left(2m\ u\cos\theta\right)\left(\frac{u}{2r\cos\theta}\right) = \frac{mu^2}{r}$$

Note that this force is the negative of the centrally directed force needed to maintain an object of mass m in uniform circular motion of radius r at speed u. A molecule just skating around the circumference of the container (such that θ approaches 90°) executes such motion.

d) F_{wall} in part **c)** is the force exerted on the wall by a single molecule. The force from N molecules is the sum of N such contributions

$$F = \sum_{N} \frac{m\ u^2}{r} = N\frac{m\overline{u^2}}{r}$$

The overbar signifies the average of the squares of the individual speeds of the N molecules. The volume V of the sphere is $\tfrac{4}{3}\pi r^3$; the surface area A of the sphere is $4\pi r^2$. The pressure exerted by N molecules is

$$P = \frac{F}{A} = \frac{Nm\overline{u^2}}{4\pi r^2\left(r\right)} \quad \text{Multiplying } P \text{ by } V \text{ gives} \quad PV = \left(\frac{Nm\overline{u^2}}{4\pi r^2\left(r\right)}\right)\left(\frac{4}{3}\pi r^3\right) = \frac{1}{3}Nm\overline{u^2}$$

9.80

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

$$F(R) = \frac{-dV_{\text{LJ}}}{dR} = \frac{4\in}{\sigma}\left[12\left(\frac{\sigma}{R}\right)^{13} - 6\left(\frac{\sigma}{R}\right)^{7}\right] = \frac{24\in}{\sigma}\left[2\left(\frac{\sigma}{R}\right)^{13} - \left(\frac{\sigma}{R}\right)^{7}\right]$$

Substitute $s = 3.40$ Å and $\in = 1.654\times10^{-21}$ J, the LJ parameters for Ar

$$F(R) = \left(1.168\times10^{-10}\text{ J m}^{-1}\right)\left[2\left(\frac{3.40\text{ Å}}{R}\right)^{13} - \left(\frac{3.40\text{Å}}{R}\right)^{7}\right]$$

$$\text{at } R = 3.0\text{ Å},\ F(R) = 9.08\times10^{-10}\text{ J m}^{-1} \quad \text{at } R = 3.4\text{ Å}, F(R) = 1.17\times10^{-10}\text{ J m}^{-1}$$

$$\text{at } R = 3.8\text{ Å}, F(R) = 1.40\times10^{-12}\text{ J m}^{-1} \quad \text{at } R = 4.2\text{ Å}, F(R) = 1.16\times10^{-11}\text{ J m}^{-1}$$

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

9.82 The rate of collision of methane molecules with the wall is

$$Z_{\text{w}} = \frac{1}{4}\frac{N}{V}\sqrt{\frac{8RT}{\pi\mathcal{M}}}A \quad \text{or} \quad Z_{\text{w}} = \frac{1}{4}\frac{n}{V}\sqrt{\frac{8RT}{\pi\mathcal{M}}}A$$

The first equation (text equation 9.24) gives the rate in molecules per second. The second gives the rate in moles per second. Combine the second version with the ideal-gas law

$$Z_{\text{w}} = \frac{1}{4}\left(\frac{P}{RT}\right)\sqrt{\frac{8RT}{\pi\mathcal{M}}}A = \frac{1}{4}P\sqrt{\frac{8}{\pi\mathcal{M}RT}}A$$

All of the quantities on the right-hand side are known, including

$$P = 2000\text{ psi}\left(\frac{1\text{ atm}}{14.696\text{ psi}}\right)\left(\frac{10132\text{ Pa}}{1\text{ atm}}\right) = 1.38\times10^{7}\text{ Pa}$$

$$\mathcal{M} = 16.04\times10^{-3}\text{ kg mol}^{-1} \quad A = 1.0\text{ mm}^2 = 1.0\times10^{-6}\text{ m}^2$$

Substitution gives the collision rate

$$Z_{\text{w}} = \frac{1}{4}\left(1.38\times10^{7}\text{ Pa}\right)\sqrt{\frac{8}{\pi\left(0.01604\text{ Kg mol}^{-1}\right)\left(8.315\text{ J K}^{-1}\text{mol}^{-1}\right)\left(293\text{ K}\right)}}\left(1.0\times10^{-6}\text{ m}^2\right)$$

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

Assume that this rate does not drop significantly because of the loss of gas through the hole. Then, the mass of methane that leaks out in one day is

$$m_{\text{CH}_4\text{ lost}} = (1\text{ d})\left(\frac{0.88\text{ mol}}{\text{s}}\right)\left(\frac{86400\text{ s}}{\text{d}}\right)\left(\frac{16.04\text{ g CH}_4}{\text{mol}}\right) = 1.2\times10^{6}\text{g}$$

The pressure and temperature of the methane in the tank are 1.38×10^7 Pa (as just computed) and 293 K. Now obtain the volume and chemical amount of the methane

$$V_{CH_4} = \pi r^2 h = \pi(20\ \text{ft})^2(50\ \text{ft})\left(\frac{0.3048^3\ \text{m}^3}{\text{ft}^3}\right) = 1.78\times10^3\,\text{m}^3$$

$$n_{CH_4} = \frac{P_{CH_4}V_{CH_4}}{RT_{CH_4}} = \frac{(1.38\times10^7\ \text{Pa})(1.78\times10^3\ \text{m}^3)}{(8.315\ \text{J K}^{-1}\ \text{mol}^{-1})(293\ \text{K})} = 1.01\times10^7\ \text{mol}$$

The fraction of the methane that escapes in one day is

$$f_{CH_4\ \text{lost}} = \frac{n_{CH_4\ \text{lost}}}{n_{CH_4}} = \frac{(1\ \text{d})(0.88\ \text{mol s}^{-1})(86\,400\ \text{s d}^{-1})}{1.01\times10^7\,\text{mol}} = 0.0075$$

9.84 **a)** If the $NH_3/N_2/O_2$ mixture is an ideal gas, then $N/V = n\,N_A/V = N_A(P/RT)$. Use text equation 9.33 to estimate the diffusion constant of NH_3 under the given conditions

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

$$= \frac{3}{8}\sqrt{\frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(293\ \text{K})}{\pi(0.017\ \text{kg mol}^{-1})}}\frac{(82.057\times10^{-6}\text{m}^3\text{atm mol}^{-1}\text{K}^{-1})(293\ \text{K})}{(3\times10^{-10}\text{m})^2(6.022\times10^{23}\text{mol}^{-1})(1\ \text{atm})}$$

$$= \frac{3}{8}(213.57\ \text{m s}^{-1})(4.436\times10^{-7}\text{m}) = 3.6\times10^{-5}\ \text{m}^2\ \text{s}^{-1}$$

b) It takes a long time for the NH_3 to diffuse 100 meters

$$t = \frac{\overline{\Delta r^2}}{6D} = \frac{(100\ \text{m})^2}{6(3.6\times10^{-5}\text{m}^2\ \text{s}^{-1})} = 4.6\times10^7\text{s} = 1.5\ \text{yr}$$

9.86 **a)** Convert the number density to density in moles per liter

$$\frac{n}{V} = \frac{10\ \text{atoms}}{1\ \text{cm}^3}\times\frac{1\ \text{mol}}{6.022\times10^{23}\ \text{atoms}}\times\frac{1000\ \text{cm}^3}{1\ \text{L}} = 1.66\times10^{-20}\text{mol L}^{-1}$$

Substitution of this value into $P = (n/V)RT$ gives $P = 1.4\times10^{-19}$atm.
b) Calculate u_{rms}

$$u_{\text{rms}} = \sqrt{\frac{3\,RT}{\mathcal{M}}} = \sqrt{\frac{3(8.3145\ \text{J K}^{-1}\text{mol}^{-1})(100\ \text{K})}{0.001008\ \text{kg mol}^{-1}}} = 1.57\times10^3\ \text{m s}^{-1}$$

Multiplying this speed by the average time between collisions gives the average distance between collisions. It is 1.57×10^{12} m, about 10.5 times the distance between Earth and Sun.

9.88 **a)** Text equation 9.30 gives the rate at which a single molecule in a gas collides with others. Substitute the various constants, the given T, P and the molar mass of methane. Then substitute 3.82×10^{-10} m, the Lennard-Jones s for methane, for d

$$Z_1 = 4\frac{N}{V}d^2\sqrt{\frac{\pi RT}{\mathcal{M}}} = 4\left(\frac{N_A P}{RT}\right)d^2\sqrt{\frac{\pi RT}{\mathcal{M}}}$$

$$= 4\left(\frac{6.022\times10^{23}\text{mol}^{-1}(101325\text{ Pa})}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}\right)d^2\sqrt{\frac{\pi(8.3145\text{ J K}^{-1}\text{mol}^{-1})(298\text{ K})}{0.01604\text{ Kg mol}^{-1}}}$$

$$= 4(2.463\times10^{25}\text{m}^{-3})(3.82\times10^{-10}\text{m})^2(696.6\text{ ms}^{-1}) = 1.00\times10^{10}\text{s}^{-1}$$

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

9.90 By Avogadro's principle

$$\frac{V_{Cl_2}}{V_{cmpd}} = \frac{0.688\text{ L}}{0.153\text{ L}} = \frac{n_{Cl_2}}{n_{cmpd}} = 4.5 \quad \text{hence} \quad \frac{n_{Cl}}{n_{cmpd}} = 9.0$$

Obtain the chemical amount of the compound using the ideal-gas law. Then get its molar mass

$$n_{cmpd} = \frac{PV_{cmpd}}{RT} = \frac{(1.00\text{ atm})(0.153\text{ L})}{(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})(273.15\text{ K})} = 6.83\times10^{-3}\text{mol}$$

$$\mathcal{M}_{cmpd} = \frac{m_{cmpd}}{n_{cmpd}} = \frac{2.842\text{ g}}{6.83\times10^{-3}\text{mol}} = 416\text{ g mol}^{-1}$$

Subtracting 9 × 35.453 g mol^{-1} for the 9 mol of Cl leaves 97.3 g mol^{-1}. Dividing by the molar mass of B, 10.811 g mol^{-1}, gives 9.0. The formula is B_9Cl_9. Compare this problem to problem **2.56**.

9.92 **a)** The reaction is $Rb_2SO_3 + 2\,HBr \rightarrow 2\,RbBr + H_2O + SO_2$. Initially

$$n_{Rb_2SO_3} = \frac{6.24\text{ g}}{251.0\text{ g mol}^{-1}} = 0.02486\text{ mol}$$

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

1 mol of Rb_2SO_3 consumes 2 mol of HBr; the HBr is 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 of RbBr is

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

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

Chapter 10

Solids, Liquids, and Phase Transitions

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

10.4 **a)** The density of this substance is $(57.9/18.3)\text{g L}^{-1} = 0.00316 \text{ g cm}^{-3}$. Although the conditions of temperature and pressure are not given, it is hard to imagine a solid or liquid ever having such a low density. The key to the problem is the knowledge of typical densities such as those of ice and water (approximately 0.9 and 1.0 g cm^{-3}).
b) The molar volume is the volume occupied by one mole of a substance. In this case:

$$V_{\text{m}} = \left(\frac{123 \text{ g}}{1 \text{ mol}}\right) \times \left(\frac{18.3 \times 10^3 \text{ cm}^3}{57.9 \text{ g}}\right) = 3.83 \times 10^4 \frac{\text{cm}^3}{\text{mol}}$$

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

10.6 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 283.15 K to 343.15 K. This substance in fact decreases its volume to 0.816 of its original value. It is a near-ideal gas.

10.8 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.

10.10 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).

10.12 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.

10.14 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.

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

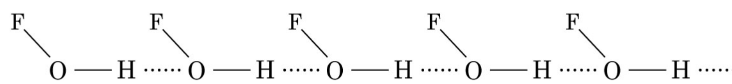
10.18 An atom of argon should be most strongly attracted by an atom of krypton. The krypton atom has more electrons and is more polarizable than one of argon and the strength of dispersion forces depends on the polarizability of the interacting species.

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

10.22 The strength of attractive forces increases with increasing molar mass. 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; the pentafluoride with the smallest molar mass (ClF_5) is the gas.

10.24 He < Ar < SO_2 < HF < CaF_2. Ar is heavier than He, while SO_2 has a dipole moment. Particularly strong dipole-dipole forces (hydrogen bonds) are present in HF, while CaF_2 is bound by ionic forces.

10.26 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.



10.28 Liquid hydrogen peroxide will have extensive hydrogen bonding and display anomalies similar to those displayed by water. It should have a higher boiling point than $F_2(l)$ and $H_2S(l)$.

10.30 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_A and $2N_A$.

10.32 Assume that helium vapor in equilibrium with liquid helium can be described by the ideal-gas equation. Then

$$V = \frac{nRT}{P} = \frac{(1.000\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})2.20\text{ K}}{0.05256\text{ atm}} = 3.43\text{ L}$$

Even at these extreme conditions, the molar volume remains large, a characteristic of a gas. The molar volume is, however, only a fraction of that at STP, 22.4 L mol^{-1}.

10.34 Treat tungsten vapor as an ideal gas.

$$\frac{n_W}{V} = \frac{P}{RT} = \frac{7.0\times10^{-9}\text{ atm}}{(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})\,2773\text{ K}} = 3.08\times10^{-11}\text{mol L}^{-1}$$

$$\frac{N_W}{V} = 3.07\times10^{-11}\text{mol L}^{-1}\times\frac{6.022\times10^{23}\text{atoms}}{\text{mol}}\times\frac{1\text{ L}}{10^3\text{ cm}^3} = 1.9\times10^{10}\text{atoms cm}^{-3}$$

10.36 The partial pressure of the hydrogen is the total pressure minus the vapor pressure of water at this temperature

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

The chemical amount and mass of hydrogen in a 1.000 L sample of the wet hydrogen are

$$n_{H_2} = \frac{PV}{RT} = \frac{(0.09587 \text{ atm})(1.000 \text{ L})}{(0.082057 \text{ L atm mol}^{-1}\text{K}^{-1})(298.15 \text{ K})} = 0.039186 \text{ mol H}_2$$

$$m_{H_2} = (0.039186 \text{ mol H}_2)(2.01588 \text{ g mol}^{-1}) = 0.0790 \text{ g H}_2$$

10.38 Assume ideal gases in an ideal mixture

$$n_{NH_3} = 3.68 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.491 \text{ g NH}_4\text{Cl}} \times \frac{1 \text{ mol NH}_3}{1 \text{ g NH}_4\text{Cl}} = 0.06880 \text{ mol NH}_3$$

$$V_{NH_3} = \frac{nRT}{P} = \frac{0.06880 \text{ mol}(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(303.15 \text{ K})}{(0.9884 - 0.0419)\text{atm}} = 1.81 \text{ L}$$

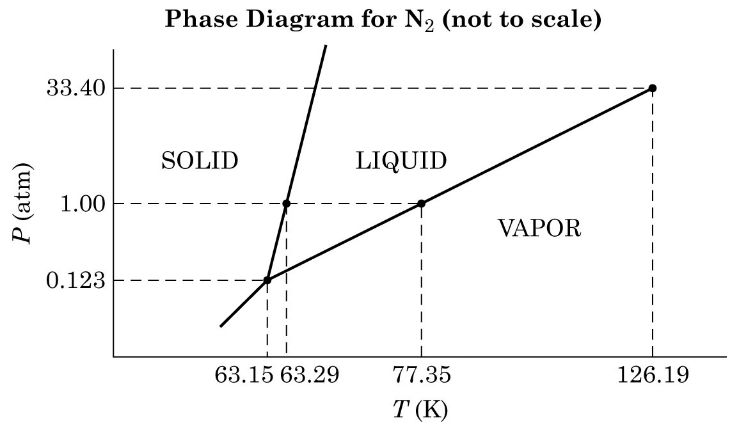
This is also the volume of the ammonia/water mixture. The two gases effectively interpenetrate (Dalton's law of partial pressure).

10.40 In text Figure 10.23c, read across on the P = 4 atm line to the liquid/vapor equilibrium line and then down to the temperature axis gives an estimate of 420 K or 147°C for the boiling point of water in the pressure cooker.

10.42 The interatomic forces in aluminum are stronger because it melts and boils higher than thallium. The vapor pressure of thallium should be higher than that of aluminum at room temperature.

10.44 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 of the tin to white tin. In order to restore the gray allotrope the temperature must be adjusted in the direction that favors gray tin, that is, the temperature must be lowered below 13.2°C.

10.46 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.



10.48 **a)** The phase diagram of H_2O (text Figure 10.21) confirms that in equilibrium at room temperature (the starting conditions 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.

10.50 **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.

10.52 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

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

10.54 The point of the problem is not the calculations, which involve nothing more than substitution into a 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 $O_2(g)$: $\Delta r = \sqrt{6D\Delta t} = \sqrt{6(2.1\times10^{-5} \text{ m}^2 \text{ s}^{-1})3600 \text{ s}} = 0.67 \text{ m}.$

b) For $H_2O(l)$: $\Delta r = \sqrt{6D\Delta t} = \sqrt{6(2.26\times10^{-9} \text{ m}^2 \text{ s}^{-1})3600 \text{ s}} = 0.0070 \text{ m}.$

c) For $Na(s)$: $\Delta r = \sqrt{6D\Delta t} = \sqrt{6(5.8\times10^{-13} \text{ m}^2 \text{ s}^{-1})3600 \text{ s}} = 0.00011 \text{ m}.$

10.56 Compute the ratio a/b for the four substances

$$\frac{a}{b} = \frac{1.390 \text{ atm L}^2 \text{ mol}^{-2}}{0.03913 \text{ L mol}^{-1}} = 35.52 \text{ L atm mol}^{-1} \quad \text{for N}_2$$
$$\frac{a}{b} = \frac{0.2444 \text{ atm L}^2 \text{ mol}^{-2}}{0.02661 \text{ L mol}^{-1}} = 9.185 \text{ L atm mol}^{-1} \quad \text{for H}_2$$
$$\frac{a}{b} = \frac{6.714 \text{ atm L}^2 \text{ mol}^{-2}}{0.05636 \text{ L mol}^{-1}} = 119.1 \text{ L atm mol}^{-1} \quad \text{for SO}_2$$
$$\frac{a}{b} = \frac{3.667 \text{ atm L}^2 \text{ mol}^{-2}}{0.04081 \text{ L mol}^{-1}} = 89.86 \text{ L atm mol}^{-1} \quad \text{for HCl}$$

The ranking is $SO_2 > HCl > N_2 > H_2$.

10.58 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 the sample is unchanged 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.

10.60 Assume that the tungsten vapor is an ideal gas (a very good assumption at this exceedingly low pressure)

$$\left(\frac{V}{n}\right)_W = \frac{RT}{P} = \frac{\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(1273 \text{ K}\right)}{2\times10^{-25}\text{atm}} = 5.2\times10^{26} \text{ L mol}^{-1}$$
$$\left(\frac{V}{N}\right)_W = \left(\frac{5.2\times10^{26} \text{ L}}{1 \text{ mol}}\right) = \left(\frac{1 \text{ mol}}{6.022\times10^{23} \text{ atoms}}\right) = 9\times10^2 \frac{\text{L}}{\text{atom}}$$

10.62 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. Assuming ideality

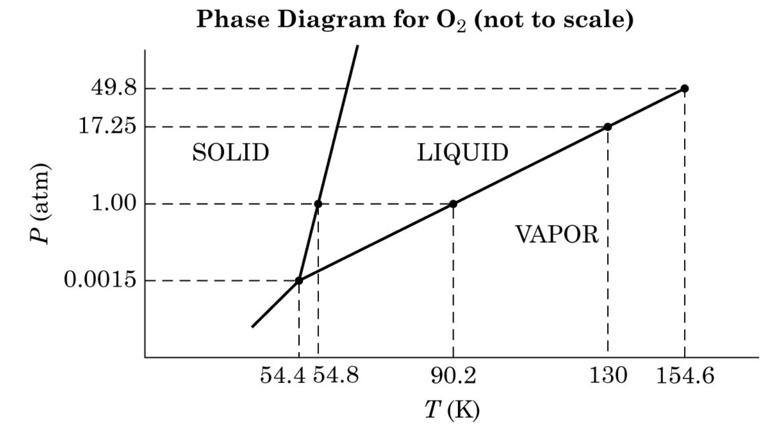
$$n_{\text{air}} = \frac{PV}{RT} = \frac{\left(1.000 \text{ atm}\right)\left(3.75 \text{ L}\right)}{\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(223.15 \text{ K}\right)} = 0.2048 \text{ mol}$$
$$P_{\text{air}} = \frac{n_{air}RT}{V}$$
$$P_{\text{air}} = \frac{\left(0.2048 \text{ mol}\right)\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(298.15 \text{ K}\right)}{6.00 \text{ L}} = 0.835 \text{ atm}$$

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

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

10.64 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 M of butane is 58.1 g mol^{-1}). This is about 1/200 of the butane in a standard lighter.

10.66



10.68 **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

$$P = \frac{F}{A} = \frac{ma}{A} = \frac{(75\text{ kg})(9.8\text{ m s}^{-2})}{8.0\times10^{-5}\text{ m}^2} = 9.2\times10^6\text{ Pa}$$

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

10.70 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.

10.72 Take $(3.4\times10^{-10}\text{ m})/2$ as the radius of an argon atom, because $(3.4\times10^{-10}\text{ m})$ is the distance at which two atoms of atom begin to repel each other. The slope of a plot of the potential energy *V (R)* of a pair of argon atoms versus the distance between the atoms becomes negative at this distance in text Figure 9.18. The volume of one argon atom is then

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(1.7\times10^{-10}\text{ m}\right)^3 = 2.06\times10^{-29}\text{ m}^3$$

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

$$V = \left(6.022\times10^{23}\right)\left(2.06\times10^{-29}\text{ m}^3\right) = 1.24\times10^{-5}\text{ m}^3$$

The fractional volume occupied is then

$$\frac{1.25\times10^{-5}\text{ m}^3}{(24.0\text{ L})\left(10^{-3}\text{ m}^3\text{ L}^{-1}\right)} = 5.2\times10^{-4}$$

Chapter 11

Solutions

11.2 Convert the given amount of C_2H_5OH from grams to moles and the volume of blood from deciliters to liters

$$c_{C_2H_5OH} = \frac{0.10 \text{ g } C_2H_5OH}{1 \text{ dL}} \times \left(\frac{10 \text{ dL}}{1 \text{ L}}\right) \times \left(\frac{1 \text{ mol } C_2H_5OH}{46.1 \text{ g } C_2H_5OH}\right) = 0.022 \text{ mol L}^{-1}$$

11.4 **a)** Consider exactly 1 L of the solution. This volume of solution contains 205.0 g of acetic acid and 820.0 g of water. It has a total mass of 1025.0 g. Use the definition of density

$$d_{\text{solution}} = \frac{m_{\text{solution}}}{V_{\text{solution}}} = \frac{1025.0 \text{ g}}{1000 \text{ cm}^3} = 1.0250 \text{ g cm}^{-3}$$

b) Continue to consider 1 L of the solution. Use the molar masses of acetic acid and water to obtain the chemical amounts of the two

$$n_{CH_3COOH} = \frac{205.0 \text{ g}}{60.05 \text{ g mol}^{-1}} = 3.4138 \text{ mol} \quad n_{H_2O} = \frac{820.0 \text{ g}}{18.015 \text{ g mol}^{-1}} = 45.518 \text{ mol}$$

Apply the definitions of the different measures of composition. Note the use of c to represent "amount concentration" (molarity) and w to represent the mass fraction of a component in a solution. These are the current recommended symbols for these quantities.

$$c_{CH_3COOH} = \frac{n_{CH_3COOH}}{\text{L solution}} = \frac{3.4138 \text{ mol}}{1.0000 \text{ L solution}} = 3.414 \text{ mol L}^{-1}$$

$$m_{CH_3COOH} = \frac{n_{CH_3COOH}}{\text{kg solvent}} = \frac{3.4138 \text{ mol}}{0.8200 \text{ kg } H_2O} = 4.163 \text{ mol kg}^{-1}$$

$$X_{CH_3COOH} = \frac{n_{CH_3COOH}}{n_{H_2O} + n_{CH_3COOH}} = \frac{3.4138 \text{ mol}}{45.518 \text{ mol} + 3.4138 \text{ mol}} = 0.06977$$

$$w_{CH_3COOH} = \frac{m_{CH_3COOH}}{m_{H_2O} + m_{CH_3COOH}} = \frac{205.0 \text{ g}}{820.0 \text{ g} + 205.0 \text{ g}} = 0.2000$$

$$\text{mass percent}_{CH_3COOH} = w_{CH_3COOH} \times 100\% = 20.00\%$$

c) Re-apply the definitions of the different measures of composition

$$c_{H_2O} = \frac{n_{H_2O}}{\text{L solution}} = \frac{45.518 \text{ mol}}{1.0000 \text{ L solution}} = 45.518 \text{ mol L}^{-1}$$

$$m_{H_2O} = \frac{n_{H_2O}}{\text{kg solvent}} = \frac{45.518 \text{ mol}}{0.2050 \text{ kg } CH_3COOH} = 222.0 \text{ mol kg}^{-1}$$

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{CH_3COOH}} = \frac{45.518 \text{ mol}}{3.4138 \text{ mol} + 45.518 \text{ mol}} = 0.9302$$

$$w_{H_2O} = \frac{m_{H_2O}}{m_{H_2O} + m_{CH_3COOH}} = \frac{820.0 \text{ g}}{820.0 \text{ g} + 205.0 \text{ g}} = 0.8000$$

$$\text{mass percent}_{H_2O} = w_{H_2O} \times 100\% = 80.00\%$$

11.6 One liter has a mass of 1171 g and it contains 1.241 mol $AgNO_3$. Then

$$m_{AgNO_3} = (1.241 \text{ mol } AgNO_3)(169.873 \text{ g mol}^{-1}) = 210.8 \text{ g}$$

$$m_{H_2O} = (1171 - 210.8) \text{ g} = 960.2 \text{ g}$$

$$m_{AgNO_3} = \frac{1.241 \text{ mol } AgNO_3}{0.9602 \text{ kg } H_2O} = 1.29 \text{ mol kg}^{-1}$$

Note the possibility of confusion from the use of m to signify both mass and molality.

11.8 The mass of the 1.00 L of water/methane solution is 780 g. The molar masses of these two substances are

$$\mathcal{M}_{CH_4} = 16.04 \text{ g mol}^{-1} \quad \mathcal{M}_{H_2O} = 18.02 \text{ g mol}^{-1}$$

Let x equal the mass of water in the solution and y equal the mass of methane. Then

$$x + y = 780 \text{ g}$$

Also, according to the definition of mole fraction

$$X_{H_2O} = \frac{x/18.02}{(x/18.02) + (y/16.04)} = 6.0 \times 10^{-5}$$

Solving these two simultaneous equations gives x = 0.053 g. This mixture is quite dilute in the solute water. Some algebraic labor can be saved by omitting the term in x in the denominator; it is quite small compared to the term in y.

11.10 **a)** Consider a 1 kg sample of the perchloric acid solution. It contains 600 g of $HClO_4$. Dividing 600 g by 100.46 g mol^{-1}, the molar mass of $HClO_4$, establishes that the solution contains 5.973 mol $HClO_4$ per kg. It simultaneously contains 9.20 mol of $HClO_4$ per liter (its molarity). Dividing the second of these two measures of composition by the first gives a density. To do the division, invert the divisor and multiply

$$\rho = \left(\frac{9.20 \text{ mol } HClO_4}{1 \text{ L solution}}\right) \times \left(\frac{1 \text{ kg solution}}{5.973 \text{ mol } HClO_4}\right) = 1.54 \text{ kg L}^{-1} = 1.54 \text{ g mL}^{-1}$$

b) To prepare 1.00 L of a solution that contains 1.00 mol of the solute requires 1.00 mol of the $HClO_4$. The 9.20 M solution is quite concentrated: 1000 mL of it supplies 9.20 mol of $HClO_4$. It follows that 1000/9.20 = 108.7 mL of solution supplies 1.00 mol of solute.

11.12 The 0.400 L sample contains $0.400\text{ L}\times 0.0700\text{ mol L}^{-1} = 0.0280\text{ mol HNO}_3$; the 0.800 L sample contains $0.800\text{ L}\times 0.0300\text{ mol L}^{-1} = 0.0240\text{ mol HNO}_3$. The solution that results, after mixing, contains 0.0520 mol HNO_3. Assume that the volume after mixing is 0.800 + 0.400 = 1.200 L. The concentration is then 0.0520 mol/1.200 L or 0.0433 mol L^{-1}. Note the assumption that the volumes of the two solutions are additive. This is not always defensible, but is justified in the case of dilute aqueous solutions such as these two.

11.14 Net ionic equations omit all ions not specifically reacting:

a) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
b) $3\ Cl_2(g) + 6\ OH^-(aq) \rightarrow ClO_3^-(aq) + 5\ Cl^-(aq) + 3\ H_2O(l)$
c) $Hg_2^{2+}(aq) + 2I^-(aq) \rightarrow Hg_2I_2(s)$
d) $3\ OCl^-(aq) + I^-(aq) \rightarrow IO_3^-(aq) + 3\ Cl^-(aq)$

11. 16

$$n_{Ca_5(PO_4)_3F} = \left(\frac{2200\times 10^3\text{ g}}{504.3\text{ g mol}^{-1}}\right) = 4.36\times 10^3\text{ mol}$$

$$n_{H_3PO_4} = 4.63\times 10^3\text{ mol Ca}_5(\text{PO}_4)_3\text{F}\left(\frac{3\text{ mol H}_3\text{PO}_4}{1\text{ mol Ca}_5(\text{PO}_4)_3\text{F}}\right) = 1.31\times 10^4\text{ mol}$$

$$V_{\text{solution}} = \frac{1.31\times 10^4\text{ mol H}_3\text{PO}_4}{6.3\text{ mol H}_3\text{PO}_4\text{L}^{-1}} = 2.1\times 10^3\text{ L}$$

11.18

$$n_{NO} = \frac{PV}{RT} = \frac{(0.970\text{ atm})(5.00\text{ L})}{(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})(20+273.15)\text{K}} = 0.2016\text{ mol NO}$$

$$n_{NaNO_2} = 0.2016\text{ mol NO}\times\frac{6\text{ mol NaNO}_2}{4\text{ mol NO}} = 0.3024\text{ mol NaNO}_2$$

$$V_{\text{solution}} = 0.3024\text{ mol NaNO}_2\times\frac{1\text{ L}}{0.646\text{ mol NaNO}_2} = 0.468\text{ L}$$

11.20 **a)** $2\ NaOH + H_2SO_3 \rightarrow 2\ H_2O + Na_2SO_3$.

This reaction involves the base sodium hydroxide, the acid sulfurous acid, and the salt sodium sulfite.

b) $Ca(OH)_2 + 2C_6H_5COOH \rightarrow 2H_2O + Ca(C_6H_5COO)_2$

This reaction involves the base calcium hydroxide, the acid benzoic acid, and the salt calcium benzoate.

c) $Pb(OH)_2 + H_2SO_4 \rightarrow 2H_2O + PbSO_4$.

This reaction involves the base lead(II) hydroxide, sulfuric acid, and the salt lead(II) sulfate.

d) $Cu(OH)_2 + 2HCl \rightarrow 2H_2O + CuCl_2$.

This reaction involves the base copper(II) hydroxide, hydrochloric acid, and the salt copper(II) chloride.

11.22 The salt comes from sodium hydroxide and sulfuric acid, so it is sodium sulfate (Na_2SO_4). The answer sodium hydrogen sulfate ($NaHSO_4$) is marginally possible, but the context suggests the complete neutralization of the sulfuric acid.

11.24 **a)** $PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5HCl.$

b)

$$n_{PCl_5} = \frac{PV}{RT} = \frac{(0.962\ \text{atm})(1.22\ \text{L})}{(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(215+273.15)\text{K}} = 0.0293\ \text{mol PCl}_5$$

$$n_{HCl} = 0.0293\ \text{mol PCl}_5 \times \frac{5\ \text{mol HCl}}{1\ \text{mol PCl}_5} = 0.1465\ \text{mol HCl} = 0.146\ \text{mol HCl}$$

$$n_{H_3PO_4} = 0.0293\ \text{mol PCl}_5 \times \frac{1\ \text{mol H}_3\text{PO}_4}{1\ \text{mol PCl}_5} = 0.0293\ \text{mol H}_3\text{PO}_4$$

Both acids are collected in enough water so that the final volume of the solution is 697 mL

$$c_{HCl} = \frac{0.1465\ \text{mol}}{0.697\ \text{L}} = 0.210\ \text{mol L}^{-1} \qquad c_{H_3PO_4} = \frac{0.0293\ \text{mol}}{0.697\ \text{L}} = 0.0420\ \text{mol L}^{-1}$$

11.26 Assume that bases other than ammonia are absent. Hydrochloric acid and ammonia react in a 1:1 molar ratio Therefore, the chemical amount of hydrochloric acid required to bring the ammonia-containing cleaning solution to the end-point (very nearly) equals the chemical amount of ammonia originally present. The chemical amount of HCl is

$$n_{HCl} = 0.8381\ \text{mol L}^{-1} \times 0.02318\ \text{L} = 0.01943\ \text{mol}$$

This much ammonia was present in 50.0 mL of the cleaning solution. Therefore, the concentration of ammonia in the cleaning solution is

$$c_{NH_3} = \frac{0.01943\ \text{mol}}{0.0500\ \text{L}} = 0.389\ \text{mol L}^{-1}$$

11.28 **a)** Nitrogen changes oxidation state from +4 in N_2O_4 to +3 in NOCl and +5 in KNO_3.

b) Sulfur changes oxidation state from −2 in H_2S to +6 in SF_6. Oxygen changes oxidation state from +1 in O_2F_2 to 0 in O_2.

c) Phosphorus changes oxidation state from +5 in $POBr_3$ to +2 in PO. Magnesium changes from 0 in Mg to +2 in $MgBr_2$.

d) Some of the chlorine changes oxidation state from −1 in BCl_3 to 0 in Cl_2. Sulfur changes from +4 in SF_4 to +2 in SCl_2.

11.30 In the equation the iodine is in the +5 oxidation state on the left side of the equation and ends up in the 0 oxidation state on the right side. Carbon is in the +2 oxidation state on the left side and goes to the +4 oxidation state on the right. All oxygen stays in the −2 oxidation state throughout the reaction. I_2O_5 is reduced. CO is oxidized.

11.32 In acidic solution, H_3O^+ and H_2O may be added either as reactants or as products to achieve balance.

a) $8\ MnO_4^-(aq) + 5\ H_2S(aq) + 14\ H_3O^+(aq) \rightarrow 8\ Mn^{2+}(aq) + 5\ SO_4^{2-}(aq) + 26\ H_2O(l)$

b) $4Zn(s) + NO_3^-(aq) + 10\ H_3O^+(aq) \rightarrow 4\ Zn^{2+}(aq) + NH_4^+(aq) + 13\ H_2O(l)$

c) $5\ H_2O_2(aq) + 2\ MnO_4^-(aq) + 6\ H_3O^+(aq) \rightarrow 5\ O_2(g) + 2\ Mn^{2+}(aq) + 14\ H_2O(l)$

d) $2\ Sn(s) + 2\ NO_3^-(aq) + 10\ H_3O^+(aq) \rightarrow 2\ Sn^{4+}(aq) + N_2O(g) + 15\ H_2O(l)$

e) $3\ UO_2^{2+}(aq) + Te(s) + 4\ H_3O^+(aq) \rightarrow 3\ U^{4+}(aq) + TeO_4^{2-}(g) + 6\ H_2O(l)$

11.34 In basic solution, OH^- and H_2O may take part either as reactants or as products.

a) $3\ OCl^-(aq) + I^-(aq) \rightarrow IO_3^-(aq) + 3\ Cl^-(aq)$

b) $2\ SO_3^{2-}(aq) + 2\ Be(s) \rightarrow S_2O_3^{2-}(aq) + Be_2O_3^{2-}(aq)$

c) $3\ H_2BO_3^-(aq) + 8\ Al(s) + 8OH^-(aq) + 7\ H_2O(l) \rightarrow 3BH_4^-(aq) + 8\ H_2AlO_3^-(aq)$

d) $2\ OH^-(aq) + O_2(g) + Sb(s) \rightarrow H_2O_2(aq) + SbO_2^{2-}(aq)$

e) $2Sn(OH)_6^{2-}(aq) + Si(s) \rightarrow 2HSnO_2^-(aq) + SiO_3^{2-}(aq) + 5H_2O(l)$

11.36 The problem can be completed simply by balancing the equations by the half-reaction method.

a) oxidation: $12\ OH^-(aq) + 4\ PH_3(g) \rightarrow P_4(s) + 12\ H_2O(l) + 12\ e^-$

reduction: $12\ e^- + 16\ H_2O(l) + 4\ CrO_4^{2-} \rightarrow 4Cr(OH)_4^-(aq) + 16\ OH^-(aq)$

The second half-equation in this case can be divided through by 4 to obtain another correct half-equation.

b) oxidation: $2\ OH^-(aq) + Fe(s) \rightarrow Fe(OH)_2 + 2\ e^-$

reduction: $2\ e^- + 2\ H_2O(l) + NiO_2(s) \rightarrow Ni(OH)_2(s) + 2\ OH^-(aq)$

c) oxidation: $2\ NH_2OH(aq) + 2OH^-(aq) \rightarrow N_2(g) + 4\ H_2O(l) + 2\ e^-$

reduction: $CO_2(g) + H_2O(l) + 2\ e^- \rightarrow CO(g) + 2\ OH^-(aq)$

11.38 The disproportionation of thiosulfate ion in acidic solution is represented

$$S_2O_3^{2-}(aq) + H_3O^+(aq) \rightarrow S(s) + HSO_3^-(aq) + H_2O(l)$$

11.40 The sample of As_2O_3 $(\mathcal{M} = 197.84\ \text{g mol}^{-1})$ contains 1.097×10^{-3}mol of As_2O_3. It gives $2\times(1.097\times10^{-3})$ or 2.194×10^{-3}mol of H_3AsO_3 in solution. The titration consumes twice this chemical amount of Ce^{4+} because these two species react in a 2 : 1 molar ratio, according to the balanced equation. This amount of Ce^{4+} ion $(4.39\times10^{-3}\text{mol})$ is delivered by 0.02147 L of solution during the titration, so the concentration of Ce^{4+} ion in the titrating solution is 0.204 mol L^{-1}.

11.42 The chemical amount of maleic acid $C_4H_4O_4$, a nonvolatile solute, is 0.01551 mol. The chemical amount of diethyl ether is 1.349 mol. By definition of the mole fraction

$$X_{C_4H_4O_4} = \frac{0.01551\ \text{mol}}{1.349\ \text{mol} + 0.01551\ \text{mol}} = 0.01137$$

The vapor pressure change is

$$\Delta P = -P^\circ X_{C_4H_4O_4} = -(0.8517\ \text{atm})(0.01137) = -0.009681\ \text{atm}$$

so the vapor pressure of ether above the solution is

$$P_{\text{ether}} = 0.8517 - 0.009681\ \text{atm} = 0.8420\ \text{atm}$$

11.44 The chemical amount anthracene and the molality of anthracene in the solution are

$$n_{\text{anthracene}} = \frac{2.62 \text{ g}}{178.23 \text{ g mol}^{-1}} = 0.0147 \text{ mol} \quad m_{\text{anthracene}} = \frac{0.0147 \text{ mol}}{0.1000 \text{ kg}} = 0.147 \text{ mol kg}^{-1}$$

The boiling-point elevation constant for cyclohexane is then

$$K_{\text{b, cyclohexane}} = \frac{\Delta T}{m_{\text{anthracene}}} = \frac{0.41 \text{ K}}{0.147 \text{ mol kg}^{-1}} = 2.8 \text{ K kg mol}^{-1}$$

11.46 The dissolution of the indium-chlorine compound in tin(IV) chloride raises the boiling point of the solvent. Assume that the compound is nonvolatile. Then,

$$m_{\text{compound}} = \frac{\Delta T}{K_b} = \frac{2.2 \text{ K}}{9.43 \text{ K kg mol}^{-1}} = 0.233 \text{ mol kg}^{-1}$$

2.60 g dissolved in 50.0 g of solvent has the same molality as 52.0 g dissolved in 1.00 kg of solvent. Thus 52.0 g is equivalent to 0.233 mol, and

$$\mathcal{M}_{\text{compound}} = \frac{52.0 \text{ g}}{0.233 \text{ mol}} = 220 \text{ g mol}^{-1}$$

The probable formula is $InCl_3$.

11.48 The change in the freezing point of the solution ΔT is 937 – 962 = –25°C = –25 K. Insert this and the K_f value into the freezing-point depression equation. The result is a molality of 0.231 mol kg^{-1}. The solution also contains

$$12 \text{ g solute/0.562 kg solvent} = 21.35 \text{ g solute (kg solvent)}^{-1}$$

according to the statement of the problem. The molar mass of the unknown solute is therefore

$$\mathcal{M}_{\text{solute}} = \frac{21.35 \text{ g solute } \left(\text{kg solvent}\right)^{-1}}{0.231 \text{ mol solute } \left(\text{kg solvent}\right)^{-1}} = 92 \text{ g mol}^{-1}$$

11.50 There is 1/8 kg = 125 g NaCl per kg of solvent. This corresponds to 2.14 mol NaCl. Consequently, $m = 2 \times 2.14 = 4.28 \text{ mol kg}^{-1}$ because each NaCl gives two ions in solution.

$$\Delta T = -K_f\, m = -\left(1.86 \text{ K kg mol}^{-1}\right)\left(4.28 \text{ mol kg}^{-1}\right) = -8.0 \text{ K}$$

This means that the freezing point is –8.0°C, or 18°F.

11.52 The solution of ethanol in sulfuric acid has a molality of 0.050 mol kg^{-1} because 2.3 g of ethanol $\left(\mathcal{M} = 46 \text{ g mol}^{-1}\right)$ equals 0.050 mol of ethanol. A solution of this molality would be expected to depress the freezing point of the sulfuric acid by $6.12 \text{ K kg mol}^{-1} \times 0.050 \text{ mol kg}^{-1} = 0.306 \text{ K}$. The actual depression is 0.92 K, which is nearly exactly three times as great. Therefore, the ethanol apparently reacts to form three particles per molecule upon dissolution in sulfuric acid. This reaction has been studied. It is

$$C_2H_5OH + 2H_2SO_4 \rightarrow C_2H_5HSO_4 + HSO_4^- + H_3O^+$$

11.54

$$c_{\text{protein}} = \frac{\pi}{RT} = \frac{0.0319 \text{ atm}}{\left(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}\right)\left(293.15 \text{ K}\right)} = 0.001326 \text{ mol L}^{-1}$$

$$\mathcal{M}_{\text{protein}} = \frac{23.7 \text{ g L}^{-1}}{0.001326 \text{ mol L}^{-1}} = 1.79\times10^{4} \text{ g mol}^{-1}$$

11.56

$$\pi_{\text{protein}} = \rho g h = \left(0.789\times10^{3} \text{ kg m}^{-3}\right)\left(9.80665 \text{ m s}^{-2}\right)\left(0.263 \text{ m}\right) = 2.035\times10^{3} \text{ Pa}$$

$$c_{\text{protein}} = \frac{\pi}{RT} = \frac{2.035\times10^{3} \text{ Pa}}{\left(8.3145 \text{ J K}^{-1} \text{ mol L}^{-1}\right)\left(20+273.15\right)\text{K}} \times \frac{1 \text{ m}^{3}}{10^{3} \text{ L}} = 8.35\times10^{-4} \text{ mol L}^{-1}$$

$$\mathcal{M}_{\text{protein}} = \frac{12.5 \text{ g L}^{-1}}{8.35\times10^{-4} \text{ mol L}^{-1}} = 1.50\times10^{4} \text{ g mol}^{-1}$$

11.58 **a)** The partial pressures in air are P_{N_2} = 0.78 atm and P_{O_2} = 0.21 atm. Use Henry's law

$$X_{N_2} = \frac{P_{N_2}}{\kappa_{N_2}} = \frac{0.78 \text{ atm}}{8.57\times10^{4} \text{ atm}} = 9.10\times10^{-6}$$

$$X_{O_2} = \frac{P_{O_2}}{\kappa_{O_2}} = \frac{0.21 \text{ atm}}{4.34\times10^{4} \text{ atm}} = 4.84\times10^{-6}$$

One liter of water contains 55.5 mol water. Because the mole fractions of the dissolved gases are so small compute the amounts of dissolved gases as follows

$$n_{N_2} = X_{N_2}\left(n_{N_2} + n_{O_2} + n_{H_2O}\right) \approx X_{N_2} n_{H_2O} = \left(9.10\times10^{-6}\right)\left(55.5 \text{ mol}\right) = 5.1\times10^{-4} \text{ mol}$$

$$n_{O_2} = X_{O_2}\left(n_{N_2} + n_{O_2} + n_{H_2O}\right) \approx X_{O_2} n_{H_2O} = \left(4.84\times10^{-6}\right)\left(55.5 \text{ mol}\right) = 2.7\times10^{-4} \text{ mol}$$

b) For a given partial pressure, less helium dissolves in the diver's blood than nitrogen because helium has an intrinsically lower solubility (larger Henry's law constant) in water than nitrogen. The substitution of helium for nitrogen in breathing mixtures for divers means that a smaller amount of gas dissolves in the divers' blood. This moderates the risk of "bends."

11.60 Use the ideal-gas law to obtain the chemical amount and then the mass of methane that is expelled by boiling the methane-in-benzene solution

$$n_{CH_4} = \frac{PV}{RT} = \frac{\left(1.00 \text{ atm}\right)\left(0.510 \text{ L}\right)}{\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)\left(273.15 \text{ K}\right)} = 0.02275 \text{ mol}$$

$$m_{CH_4} = 0.02275 \text{ mol} \times \left(16.04 \text{ g mol}^{-1}\right) = 0.365 \text{ g}$$

This amount of methane was present in 1.00 kg of solution. The solution was very dilute. It contained less than half a gram of methane and 999.6 g of benzene ($\mathcal{M} = 78.114 \text{ g mol}^{-1}$), which is 12.80 mol. The mole fraction of methane is

$$X_{CH_4} = \frac{0.02275 \text{ mol}}{\left(12.80 + 0.02275\right) \text{ mol}} = 1.774\times10^{-3}$$

This fraction of methane was maintained in solution by a pressure of 1.00 atm of methane. The Henry's law constant is

$$\kappa = \frac{P_{\text{methane}}}{X_{\text{methane}}} = \frac{1.00 \text{ atm}}{1.774\times10^{-3}} = 564 \text{ atm}$$

11.62 The vapor pressure of a component in this ideal case is simply the vapor pressure that the pure component would have multiplied by its mole fraction in the solution. Therefore, the vapor pressure of the toluene above this solution is

$$P_{\text{toluene}} = X_{\text{toluene}}\, P^{\circ}_{\text{toluene}} = \left(\frac{0.900}{0.400+0.900}\right)(0.534 \text{ atm}) = 0.370 \text{ atm}$$

at this temperature, and the vapor pressure of the benzene is 0.412 atm, by a similar calculation. The total pressure of the vapors above the solution is 0.782 atm, which is the sum of the partial pressures of the two volatile components of the solution. The mole fraction of benzene in the vapor is

$$X_{\text{benzene}} = \frac{0.412 \text{ atm}}{0.782 \text{ atm}} = 0.527$$

11.64 **a)** The chemical amount of benzene $\left(\mathcal{M} = 78.11 \text{ g mol}^{-1}\right)$ in 50.0 g is 0.640 mol. The chemical amount of *n*-hexane $\left(\mathcal{M} = 86.18 \text{ g mol}^{-1}\right)$ is 0.580 mol. The mole fraction of benzene in the solution is

$$X_{\text{benzene}} = \frac{0.640 \text{ mol}}{(0.640+0.580) \text{ mol}} = 0.525$$

b) The total vapor pressure above the solution is

$$\begin{aligned} P_{\text{tot}} &= P_{\text{benzene}} + P_{\text{hexane}} \\ &= X_{\text{benzene}} P^{\circ}_{\text{benzene}} + X_{\text{hexane}} P^{\circ}_{\text{hexane}} \\ &= 0.525(0.1355 \text{ atm}) + (1-0.525)(0.2128 \text{ atm}) = 0.172 \text{ atm} \end{aligned}$$

c) $X_{\text{benzene}}(\text{vapor}) = 0.525(0.1355 \text{ atm})/0.172 \text{ atm} = 0.414$.

11.66 **a)** $Ba(NO_3)_2(amm) + 2\ AgBr(amm) \rightarrow BaBr_2(s) + 2\ AgNO_3(amm)$.

b)

$$V = 0.215 \text{ L} \times \frac{0.076 \text{ mol Ba(NO}_3)_2}{\text{L}} \times \frac{2 \text{ mol AgBr}}{\text{mol Ba(NO}_3)_2} \times \frac{1 \text{ L}}{0.50 \text{ mol AgBr}} = 0.065 \text{ L}$$

c)

$$m_{\text{BaBr}_2} = 0.215 \text{ L} \times \frac{0.076 \text{ mol Ba(NO}_3)_2}{\text{L}} \times \frac{1 \text{ mol BaBr}_2}{1 \text{ mol Ba(NO}_3)_2} \times \frac{297.14 \text{ g}}{\text{mol BaBr}_2} = 4.9 \text{ g}$$

11.68 The amount of halide ions in the 50 mL of solution is $50.0 \text{ mL} \times 0.100 \text{ mol L}^{-1} = 5.00$ mmol. If there is *x* mmol AgBr in the precipitate then there is (5.00 – *x*) mmol of AgCl, and

$$(5.00 - x)\ \text{mmol AgCl}\left(\frac{143.3\ \text{mg}}{\text{mmol AgCl}}\right) + (x)\text{mmol AgBr}\left(\frac{187.8\ \text{mg}}{\text{mmol AgBr}}\right) = 762\ \text{mg}$$

Solving for x gives 1.02 mmol AgBr. The 1.02 mmol AgBr comes from 1.02 mmol HBr. Neutralization of this much HBr requires

$$\frac{1.02\ \text{mmol}}{0.100\ \text{mol L}^{-1}} = 10.2\ \text{mL of } 0.100\ \text{M NaOH}$$

11.70 Mn(VII) is reduced to Mn(II) by antibiotic A, which is itself oxidized. Compute the number of moles of electrons that A gives up in experiment (a)

$$n_{e^-} = 0.0183\ \text{L} \times \frac{8.0 \times 10^{-2}\ \text{mol Mn(II)}}{\text{L}} \times \frac{5\ \text{mol } e^-}{\text{mol Mn(II)}} = 7.32 \times 10^{-3}\ \text{mol } e^-$$

Suppose that x mol of electrons is needed to oxidize 1 mol of antibiotic A. Then the molar mass of A is

$$\mathcal{M}_A = \frac{0.293\ \text{g}(x)}{7.32 \times 10^{-3}\ \text{mol}} = 40.0(x)\ \text{g mol}^{-1} \quad x = 1, 2, \ldots$$

This is all that can be concluded about the molar mass of A on the basis of experiment (a).

In experiment (b), antibiotic A, which is an acid, is neutralized by sodium hydroxide of known concentration. Compute the number of moles of OH^- that is used

$$n_{OH^-} = 0.0157\ \text{L} \times 0.409\ \text{mol L}^{-1} = 7.69 \times 10^{-3}\ \text{mol}$$

If a mole of A contains y mol of acidic (neutralizable) H atoms then

$$\mathcal{M}_A = \frac{0.385\ \text{g}}{7.69 \times 10^{-3}\ \text{mol}}(y) = 50.0(y)\ \text{g mol}^{-1} \quad y = 1, 2, \ldots$$

This is all that can be concluded about the molar mass of A on the basis of experiment (b).

Because A has only one molar mass, $40.0\,x = 50.0y$ from which $x/y = \frac{5}{4}$. Because x and y are both integers, the minimum molar mass of A is 200 g mol^{-1}, corresponding to $x = 5$ and $y = 4$. Larger values for the molar mass cannot be ruled out: 400 g mol^{-1}, corresponding to $x = 10$, $y = 8$; then 600 g mol^{-1}, corresponding to $x = 15$, $y = 12$, and so forth.

11.72 The second reaction uses $0.0262\ \text{L} \times 0.1359\ \text{mol L}^{-1} = 3.56 \times 10^{-3}$ mol of thiosulfate ion to consume the I_3^- ion. From the stoichiometry of the second reaction, one-half of this amount of I_3^- ion, which is 1.78×10^{-3} mol, was present. By the stoichiometry of the first reaction, the identical chemical amount of $O_3(g)$ was present in the original mixture: $n_{O_3} = 1.78 \times 10^{-3}$ mol Use the ideal-gas equation to figure out the total number of moles of gases in the original mixture. Then use the definition of mole fraction

$$n_{\text{gas}} = \frac{PV}{RT} = \frac{(0.993 \text{ atm})(53.2 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15+18)\text{K}} = 2.211 \text{ mol}$$

$$X_{\text{O}_3} = \frac{n_{\text{O}_3}}{n_{\text{gas}}} = \frac{1.78\times10^{-3} \text{ mol}}{2.211 \text{ mol}} = 8.05\times10^{-4}$$

11.74 By the definition of mole fraction, there is 39.0 mol of NaI in the solution for every 61.0 mol of water. Converting this amount of water to kilograms (using the molar mass of water) establishes that the solution has 39.0 mol of NaI per 1.0989 kg of water. This is the same as 35.5 mol of NaI per 1.00 kg of water. Assuming that the Nal is fully dissociated into ions gives an effective molality that is twice this, or 71.0 mol kg^{-1}. Inserting this molality into the standard (approximate) formula $\Delta T = K_b m$ with $K_b = 0.512$ K kg mol^{-1} gives $\Delta T = 36$ K. The experimental ΔT is 44 K.

11.76 Compute the apparent molality of the solution from the freezing point depression. It is

$$m = -\frac{\Delta T}{K_f} = -\frac{-0.99 \text{ K}}{34.3 \text{ K kg mol}^{-1}} = 0.0289 \text{ mol kg}^{-1}$$

The 1.36 g of mercury(I) chloride dissolved in 100 g of the solvent is 0.00289 mol of mercury(I) chloride and

$$\mathcal{M}_{\text{HgCl, apparent}} = \frac{1.36 \text{ g}}{0.00289 \text{ mol}} = 471 \text{ g mol}^{-1}$$

If mercury(I) chloride ionized in this solvent, then its apparent molar mass would be *less* than 236 g mol^{-1}, which is the molar mass of HgCl. Instead, the apparent molar mass is almost exactly twice this number. Instead of ionizing to give more particles the "HgCl" in this solution clusters together in dimers; it exists as Hg_2Cl_2.

11.78 The molality of the required antifreeze solution of ethylene glycol is

$$m = -\frac{\Delta T}{K_f} = -\frac{(-5.0)}{1.86} = 2.69 \text{ mol kg}^{-1}$$

Such a solution has 2.69 mol of CH_2OHCH_2OH ($\mathcal{M} = 62.07$ g mol^{-1}) dissolved in 1000 g of water. This chemical amount of ethylene glycol equals 167 g. There is thus 167 g of ethylene glycol for every 1167 g of solution. The percentage by mass of the ethylene glycol in the solution is $167/1167\times100\% = 14.3\%$. Note the assumption that ethylene glycol neither dissociates into two or more particles nor associates in aqueous solution (in addition to the assumption of ideal solution behavior).

11.80 The vapor pressure above beaker 1 is higher than it is over beaker 2. Water evaporates from beaker 1 and condenses into beaker 2 until the concentrations in the two become equal, and the vapor pressures above them also become equal. Assume that the amount of water vapor in the *small* closed container is negligible. Then

$$n_{\text{NaCl}}(\text{beaker 1}) = (0.400\text{ L})(0.100\text{ mol L}^{-1}) = 0.0400\text{ mol}$$
$$n_{\text{NaCl}}(\text{beaker 2}) = (0.200\text{ L})(0.250\text{ mol L}^{-1}) = 0.0500\text{ mol}$$
$$n_{\text{total}} = 0.0900\text{ mol NaCl}$$
$$V_{\text{total}} = 400\text{ mL} + 200\text{ mL} = 600\text{ mL water}$$
$$c_{\text{final}} = \frac{n_{\text{total}}}{V_{\text{total}}} = \frac{0.0900\text{ mol}}{600\text{ mL}} = 0.150\text{ mol L}^{-1}$$
$$V_{\text{final}}(\text{beaker 1}) = \frac{0.0400\text{ mol}}{0.150\text{ mol L}^{-1}} = 267\text{ mL}$$
$$V_{\text{final}}(\text{beaker 2}) = \frac{0.0500\text{ mol}}{0.150\text{ mol L}^{-1}} = 333\text{ mL}$$

11.82 Compute the osmotic pressure π of the solution. Then use $\pi = \rho gh$ to get the height

$$\pi = \left(\frac{n}{V}\right)RT = \left(\frac{0.010\times10^{3}\text{ mol}}{\text{m}^{-3}}\right)(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(696.15\text{ K}) = 5.79\times10^{4}\text{ Pa}$$
$$h = \frac{\pi}{\rho g} = \frac{5.79\times10^{4}\text{ Pa}}{(11.4\times10^{3}\text{ kg m}^{-3})(9.80665\text{ ms}^{-2})} = 0.52\text{ m}$$

11.84 According to problem **11.62**, the vapor pressure of toluene is 0.534 atm at 90°C, and the vapor pressure of benzene is 1.34 atm. In order for the solution to boil, the total pressure above it must equal 1.00 atm. This total pressure is the sum of the pressures of the two components, each of which is given by Raoult's law. Let the mole fraction of the toluene in solution equal X_{tol} Then the mole fraction of the benzene is $1 - X_{\text{tol}}$, and

$$(0.534\text{ atm})X_{\text{tol}} + (1.34\text{ atm})(1 - X_{\text{tol}}) = 1.00\text{ atm}$$

Solving for X_{tol} gives 0.42 as the answer

11.86 The mass of 1.000 mol of Na_2SO_4 is 142.04 g. The additional mass, 322.2 – 142.04 = 180.2 g, must be water of hydration. Its chemical amount is

$$n\text{H}_2\text{O} = \frac{180.2\text{ g}}{18.02\text{ g mol}^{-1}} = 10.0\text{ mol H}_2\text{O}$$

so the chemical formula of the solid hydrate is $Na_2SO_4 \cdot 10H_2O$.

11.88 At "the end" (equilibrium), the partial pressure of H_2O above beaker A equals the partial pressure of water above beaker B. Obviously, the mole fractions of fructose and H_2O add up to 1 in both beakers. Moreover, the mole fractions of fructose in the two beakers are equal, as the following confirms

$$\begin{aligned} P_{\mathrm{H_2O,\,A}} &= P_{\mathrm{H_2O,\,B}} \\ \left(X_{\mathrm{H_2O,\,A}}\right)P^{\circ}_{H_2O} &= \left(X_{\mathrm{H_2O,\,B}}\right)P^{\circ}_{H_2O} \\ \left(1 - X_{\text{fructose, A}}\right)P^{\circ}_{H_2O} &= \left(1 - X_{\text{fructose, B}}\right)P^{\circ}_{H_2O} \\ \left(1 - X_{\text{fructose, A}}\right) &= \left(1 - X_{\text{fructose, B}}\right) \\ X_{\text{fructose, A}} &= X_{\text{fructose, B}} \text{ at equilibrium} \end{aligned}$$

a) Abbreviate fructose with the letter f. Then $[\mathrm{f}]_{\mathrm{A}}$ and $[\mathrm{f}]_{\mathrm{B}}$ represent the molar concentrations of fructose in beakers A and B respectively. It was just shown that $X_{\mathrm{f,\,A}} = X_{\mathrm{f,\,B}}$. Therefore at the end

$$\left[\mathrm{f}\right]_{\mathrm{A}} = \left[\mathrm{f}\right]_{\mathrm{B}} = 1.5 \text{ mol L}^{-1}$$

b) The amount of fructose in each beaker is unchanged throughout. Hence

$$\left[\mathrm{f}\right]_{\text{initial, A}} = \left[\mathrm{f}\right]_{\text{final, A}}\left(\frac{V_{\text{final, A}}}{V_{\text{initial, A}}}\right) = \left(1.5 \text{ mol L}^{-1}\right)\frac{400 \text{ mL}}{600 \text{ mL}} = 1.0 \text{ mol L}^{-1}$$

c) Similarly for beaker B

$$\left[\mathrm{f}\right]_{\text{initial, B}} = \left[\mathrm{f}\right]_{\text{final, B}}\left(\frac{V_{\text{final, B}}}{V_{\text{initial, B}}}\right) = \left(1.5 \text{ mol L}^{-1}\right)\frac{300 \text{ mL}}{100 \text{ mL}} = 4.5 \text{ mol L}^{-1}$$

d) The total volume of solution does not matter for this part. Assume 1000 mL for simplicity. The mass of the solution is then 1100 g, and the mass of the solute (fructose) in thesolution is $1.5 \text{ mol L}^{-1} \times 180 \text{ g mol}^{-1} = 270 \text{ g}$. Then

$$\begin{aligned} n_{\mathrm{H_2O}} &= \frac{m_{\mathrm{H_2O}}}{\mathcal{M}} = \frac{m_{\text{solution}} - m_{\text{solute}}}{\mathcal{M}} = \frac{\left(1100 - 270\right)}{18.0 \text{ g mol}^{-1}} = 46.1 \text{ mol} \\ X_{\mathrm{H_2O}} &= \frac{n_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}} + n_{\text{fructose}}} = \frac{46.1 \text{ mol}}{46.1 \text{ mol} + 1.5 \text{ mol}} \\ P_{\mathrm{H_2O}} &= X_{\mathrm{H_2O}}P^{\circ}_{\mathrm{H_2O}} \\ P_{\mathrm{H_2O}} &= \left(\frac{46.1 \text{ mol}}{\left(1.5 + 46.1\right) \text{ mol}}\right)25.2 \text{ torr} = 24 \text{ torr} \end{aligned}$$

Chapter 12

Thermodynamic Processes and Thermochemistry

12.2 The work done in a change of volume at constant pressure is $w = -P_{ext}\Delta V$. The change in the volume is $V_2 - V_1 = 800 - 150 = 650$ mL=0.650 L, and P is 0.98 atm so $w = -0.64$ L atm. Using the fact that 1 L atm is 101.325 J, this is -65 J.

12.4 For a parcel of falling water of mass m under the stated assumptions

$$-mg\Delta h = c_s m\Delta T$$

The m cancels out. Express c_s in J K^{-1}kg^{-1} so that the units will work out correctly:

$$-\left(9.81 \text{ m s}^{-2}\right)\left(-100 \text{ m}\right) = \left(4180 \text{ J K}^{-1} \text{ kg}^{-1}\right)\Delta T \text{ from which } \Delta T = +0.235 \text{ K}$$

12.6 Molar heat capacities are specific heats multiplied by molar masses: $c_P = \mathcal{M}c_s$. Analysis of the units confirms this relationship. The molar heat capacities (at constant pressure) of the gaseous halogens come out to be:

	c_s(J K^{-1}g^{-1})	$\mathcal{M}$(g mol^{-1})	c_P(J K^{-1} mol^{-1})
F_2	0.824	38.0	31.3
Cl_2	0.478	70.9	33.9
Br_2	0.225	159.8	36.0
I_2	0.145	253.8	36.8

Molar heat capacity increases moving down the halogen group in the periodic table. The molar heat capacity of solid astatine probably lies between 37 and 38 J K^{-1}mol^{-1}.

12.8 The rule of Dulong and Petit states that the molar heat capacities (c_P) of the (solid) metallic elements equal approximately 25 J K^{-1}mol^{-1}. Use $c_s = c_P/\mathcal{M} = 25 \text{ J K}^{-1} \text{ mol}^{-1}/\mathcal{M}$. The answers are 0.49, 0.36, and 0.23 J K^{-1}g^{-1} for V, Ga and Ag, respectively.

12.10 **a)** Identify the battery (not the toy truck) as the system of interest and apply the first law to it. The battery performs 117.0 J of work on the surroundings. This means that it absorbs negative work:

$w_{\text{batt}} = -117.0$ J. The battery evolves 3.0 J to its surroundings. This means that it absorbs –3.0 J of heat: $q_{\text{batt}} = -3.0$ J. By the first law, $\Delta U_{\text{batt}} = -120.0$ J.

b) Recharging the battery puts it back the way it was before it was discharged. The final state is indistinguishable from the original, state, so $\Delta U_{\text{overall}} = 0$. For the battery

$$\begin{aligned}\Delta U_{\text{overall}} &= \Delta U_{\text{charge}} + \Delta U_{\text{discharge}}\\ 0 &= (q+w)_{\text{charge}} + (q+w)_{\text{discharge}}\\ 0 &= (q_{\text{charge}} + 210.0\text{ J}) + (-3.0\text{ J} - 117.0\text{ J})\\ q_{\text{charge}} &= -90.0\text{ J}\end{aligned}$$

The sign of q during the charge cycle is negative because the battery evolves heat to the surroundings as it is charged, probably because of resistive heating.

12.12 Assume that the water and zinc are thermally isolated from the rest of the world. Then,

$$q_{\text{water}} + q_{\text{zinc}} = 0$$
$$(c_{s,\text{water}} m_{\text{water}} \Delta t_{\text{water}}) + (c_{s,\text{zinc}} m_{\text{zinc}} \Delta t_{\text{zinc}}) = 0$$

The Δt of the zinc is (t_f – 20.0)°C and the Δt of the water is (t_f – 100.0)°C. Substitute the given specific heat capacities,[1] the masses, and the temperature changes into this equation

$$\left(4.22\text{ J}(°\text{C})^{-1}\text{ g}^{-1}\right)(200.0\text{ g})(t_f - 100.0°\text{C}) + \left(0.389\text{ J}(°\text{C})^{-1}\text{ g}^{-1}\right)(60.0\text{ g})(t_f - 20.0°\text{C}) = 0$$

Solving gives t_f = 97.8°C.

12.14 This problem can be solved by setting up an equation like the one used to solve problem **12.12**. One can also use the rule derived in problem **12.13**. In the special case of mixing equal masses of substances 1 and 2 at different temperatures

$$\frac{c_{s\,1}}{c_{s\,2}} = -\frac{\Delta t_2}{\Delta t_1}$$

In this problem, this expression becomes

$$0.10 = -\frac{(t_f - 20.0°\text{C})}{(t_f - 92.0°\text{C})}$$

The minus signs appear in these two equations because of the convention that a change in a quantity is the final value minus the initial. Solving gives t_f = 26.5°C.

12.16 Let m represent the original masses of ice and boiling water, and define the system as the mixture of the ice and boiling water. The q for the system in the insulated container is 0. Define subsystem *ice* as the part of the system that was originally ice at 0°C and subsystem *hw* as the part of the system that was originally boiling water at 100.0°C. Then

$$q_{ice} + q_{hw} = 0$$

[1] The specific heat capacities are given in units of J $K^{-1}g^{-1}$ which are equivalent to J $(°C)^{-1}g^{-1}$.

The heat absorbed by the ice as it melts is 333.4m J. The ice forms water at 0.00°C as it melts. The melted ice then absorbs heat as it rises in temperature to the "Galen temperature" t_G. This heat equals $4.184 \times m \times (t_G - 0.00)$ J. The heat absorbed by the boiling water as it cools to the Galen temperature is $4.184 \times m \times (t_G - 100.0)$ J. Hence

$$333.4m + 4.184m\left(t_G\right) + 4.184m\left(t_G - 100.0\right) = 0$$

The m divides out of this equation which is then readily solved for t_G. The answer is 10.2°C.

12.18 For the reversible cooling of a system consisting of 6.00 mol of H_2 when the pressure is held constant at 2.00 atm and the system contracts from 100 L to 50.0 L

a)

$$T_1 = \frac{PV}{RT} = \frac{\left(2.00 \text{ atm}\right)\left(100 \text{ L}\right)}{\left(6.00 \text{ mol}\right)\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)} = 406 \text{ K}$$

$$T_2 = \left(\frac{50.0 \text{ L}}{100 \text{ L}}\right)\left(406 \text{ K}\right) = 203 \text{ K}$$

b) $w = -P\Delta V = -\left(2.00 \text{ atm}\right)\left(50.0 \text{ L} - 100 \text{ L}\right) = +100 \text{ L atm} = +1.01\times10^4 \text{ J}$

c)

$$\Delta U = nc_V\Delta T = n\left(c_P - R\right)\Delta T$$

$$= \left(6.00 \text{ mol}\right)\left(29.3 - 8.3145 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(203 - 406 \text{ K}\right) = -2.56\times10^4 \text{J}$$

d) $q = \Delta U - w = -2.56\times10^4 \text{J} - 1.01\times10^4 \text{ J} = -3.57\times10^4 \text{J}$.

12.20 For an ideal gas, $\Delta U = nc_V\Delta T = 0$ if $\Delta T = 0$ (isothermal). Because P_{ext} = 0, $w = -P_{ext}\Delta V = 0$. Finally $q = \Delta U - w = 0 - 0 = 0$.

12.22 **a)** $w = -P_{ext}\Delta V = -2.00 \text{ atm}\left(10.00 - 6.00 \text{ L}\right) = -8.00 \text{ L atm} = -811 \text{ J}$

$\Delta U = q + w = +500 - 811 = -311$ J

b) $\Delta U = -311$ J because E is a function of state. However q = 0 and

$$w = \Delta U - q = -311 \text{ J} - 0 = -311 \text{ J}$$

12.24 CH_4 is a non-linear molecule with 5 atoms and 15 total degrees of freedom. Table 12.3 summarizes the predictions of the equipartition theorem. The total value of c_P = (26R/2) arising from 3 degrees of translational motion (each contributing (R/2)), 3 degrees of rotational motion (each contributing (R/2)), and 3N-6 = 15 – 6 = 9 degrees of vibrational motion contributing R for a total (24R/2) to c_V. One additional term of R must be added to obtain c_P= (26R/2). The predicted numerical value for CH_4 is c_P = 108.08 J mol^{-1} K^{-1}.

Neglecting the vibrational motion predicts c_P = (26R/2 – 9R) = (8R/2)= 33.26 J mol^{-1} K^{-1}.
The measured value is c_P = 35.31 J mol^{-1} K^{-1}. (Table 3)
The vibrational contribution = 35.31 – 33.26 = 2.05 J mol^{-1} K^{-1}.
Per Cent of c_P for CH_4 due to vibration = (2.05/35.31) x 100 = 5.8%

C_2H_4 is a non-linear molecule with 6 atoms and 18 total degrees of freedom. Table 12.3 summarizes the predictions of the equipartition theorem.. The total value of c_P = (32R/2) arising from 3 degrees of translational motion (each contributing (R/2)), 3 degrees of rotational motion (each contributing (R/2)), and 3N-6 = 18 – 6 = 12 degrees of vibrational motion contributing R for a total (30R/2) to c_V. One additional term of R must be added to obtain c_P= (32R/2). The predicted numerical value for C_2H_4 is c_P = 133.02 J mol^{-1} K^{-1}.

Neglecting the vibrational motion predicts c_P = (32R/2 – 12R) = (8R/2)= 33.26 J mol^{-1} K^{-1}. The measured value is c_P = 43.56 J mol^{-1} K^{-1}. (Table 3) The vibrational contribution = 43.56 – 33.26 = 10.30 J mol^{-1} K^{-1}. Per Cent of c_P for C_2H_4 due to vibration = (10.30/43.56) x 100 = 23.6%

12.26 Because a solid experiences very little change in volume during heating, the change in enthalpy is nearly the same as the change in internal energy, and $c_P \approx c_V$. Consequently $\Delta H \approx \Delta E = n\ c_V\ \Delta T$. The equipartition theorem predicts the molar heat capacity for elemental metals above room temperature to be c_V = 3R = 24.94 in accordance with the law of Dulong and Petit. (See Table 12.3.)

(a) The atomic mass of Al = 26.98, so 20.0 g = 0.74 mol.

$\Delta H \approx \Delta E$ = (0.741 mol)(24.794 J mol^{-1} K^{-1})(275 K) = 5, 084 J = 5.084 kJ

(b) The atomic mass of Pb = 207.2, so 20.0 g = 0.097 mol.

$\Delta H \approx \Delta E$ = (0.097 mol)(24.794 J mol^{-1} K^{-1})(275 K) = 662 J = 0.662 kJ

12.28 **a)**

$$\Delta H = \frac{-683\text{ kJ}}{1\text{ mol Br}_2} \times \frac{1\text{ mol Br}_2}{2(79.904)\text{ g Br}_2} = -4.27\text{ kJ g}^{-1}$$

b)

$$\Delta H = \frac{+472\text{ kJ}}{4\text{ mol Fe}_3\text{O}_4} \times \frac{1\text{ mol Fe}_3\text{O}_4}{231.54\text{ g Fe}_3\text{O}_4} = +0.510\text{ kJ g}^{-1}$$

c)

$$\Delta H = \frac{+806\text{ kJ}}{2\text{ mol NaHSO}_4} \times \frac{1\text{ mol NaHSO}_4}{120.06\text{ g NaHSO}_4} = +3.36\text{ kJ g}^{-1}$$

12.30 The reaction "absorbs negative heat" at constant pressure. Its q_P is –670 J. Then

$$\Delta H = -\left(\frac{-670\text{ J}}{1.00\text{ g CuCl}_2}\right) \times \left(\frac{134.452\text{ g CuCl}_2}{1\text{ mol CuCl}_2}\right) = -90.1 \times 10^3\text{ J mol}^{-1}$$

12.32 In this process NaCl(l) freezes, so the q_P of the NaCl system is negative and

$$\Delta H = \left(\frac{-28.8\text{ kJ}}{1\text{ mol NaCl}}\right) \times \left(\frac{1\text{ mol NaCl}}{58.44\text{ g NaCl}}\right) \times \left(56.2 \times 10^3\text{ g NaCl}\right) = -2.77 \times 10^4\text{ kJ}$$

12.34 The ice at 0.0°C melts to form water at 0.0°C. The water from the melted ice has $\Delta T = 0$ (absorbs no heat) and can be omitted in the heat balance.

$$0 = q_{\text{ice}} + q_{\text{water}} = \Delta H_{\text{fus}} m_{\text{ice}} + c_{s\ \text{water}} m_{\text{water}} \Delta T_{\text{water}}$$
$$0 = \left(333\ \text{J g}^{-1}\right) m_{\text{ice}} + \left(4.18\ \text{J K}^{-1}\text{g}^{-1}\right)\left(150\ \text{g}\right)\left(-25\ \text{K}\right)$$
$$m_{\text{ice}} = 47\ \text{g}$$

12.36 The reaction of interest can be constructed as three times the first reaction added to the second reaction. The enthalpy changes combine in the same way as the equations. Thus

$$\Delta H = \Delta H_2 + 3\Delta H_1 = 461.05 + 3\left(520.9\right) = +2023.8\ \text{kJ}$$

12.38 The conversion of monoclinic sulfur to rhombic sulfur can be imagined to proceed by the combustion of monoclinic sulfur to SO_2 followed by the "un-combustion" of SO_2 to rhombic sulfur. Therefore $\Delta H = -9.376 - \left(-9.293\right) = -0.083\ \text{kJ g}^{-1}$.

12.40 In every case the applicable equation is

$$\Delta H^0 = \sum_{\text{products}} \Delta H_{\text{f}}^0 - \sum_{\text{reactants}} \Delta H_{\text{f}}^0$$

Enthalpies of formation are always tabulated on a "per amount" basis. The ΔH_{f}^0's from Appendix D are given per mole of substance. Each must be multiplied by the number of moles appearing in the balanced equation.

a)

$$\Delta H_{298}^0 = 2\ \text{mol}\left(33.18 \frac{\text{kJ}}{\text{mol}}\right) - 1\ \text{mol}\left(0 \frac{\text{kJ}}{\text{mol}}\right) - 2\ \text{mol}\left(90.25 \frac{\text{kJ}}{\text{mol}}\right) = -114.14\ \text{kJ}$$

b)

$$\Delta H_{298}^0 = 2\ \text{mol}\left(-110.52 \frac{\text{kJ}}{\text{mol}}\right) - 1\ \text{mol}\left(-393.51 \frac{\text{kJ}}{\text{mol}}\right) - 1\ \text{mol}\left(0 \frac{\text{kJ}}{\text{mol}}\right) = +172.47\ \text{kJ}$$

c) Omitting the units: $\Delta H_{298}^0 = 3\left(-241.82\right) + 2\left(33.18\right) - 7/2\left(0\right) - 2\left(-46.11\right) = -566.88\ \text{kJ}$.

d) $\Delta H_{298}^0 = 1\left(0\right) + 1\left(-110.52\right) - 1\left(-241.82\right) - 1\left(0\right) = +131.30\ \text{kJ}$

The subscript "298" appears because the ΔH_{f}^0's of Appendix D are for formation reactions occurring at 298.15 K. This subscript is often omitted when the context warrants it.

12.42 **a)** The reaction is

$$2\ \text{Al}(s) + \text{Fe}_2\text{O}_3(s) \rightarrow 2\ \text{Fe}(s) + \text{Al}_2\text{O}_3(s)$$

The standard enthalpy of reaction is computed by combining the ΔH_{f}^0's from Appendix D:

$$\Delta H^0 = 2\underbrace{\left(0\right)}_{\text{Fe}(s)} + 1\underbrace{\left(-1675.7\right)}_{\text{Al}_2\text{O}_3(s)} - 2\underbrace{\left(0\right)}_{\text{Al}(s)} - 1 - \underbrace{\left(-824.2\right)}_{\text{Fe}_2\text{O}_3(s)} = -851.5\ \text{kJ}$$

b) According to the result in part **a)**, 851.5 kJ of heat is given off at constant pressure when one mole of $Fe_2O_3(s)$ reacts. One mole of Fe_2O_3 is 159.69 g, so the amount of heat given off by the reaction of 3.21 g of $Fe_2O_3(s)$ is

$$q = -851.5 \text{ kJ mol}^{-1} \times \frac{3.21 \text{ g}}{159.69 \text{ g mol}^{-1}} = -17.1 \text{ kJ}.$$

12.44 **a)** The reaction is a dissolution: $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$. Use the values in Appendix D for the ΔH_f^0 at 298 K of the two ions and solid ammonium nitrate:

$$\Delta H_{298}^0 = 1(-132.51) + 1(-205.0) - 1(-365.56) = +28.05 \text{ kJ}$$

b) Dissolving 15.0 g (0.187 mol) of NH_4NO_3 to give the ions in standard states (ideal solutions of each at a concentration of 1 M) has $\Delta H^0 = 5.26$ kJ. Here, the final concentrations of the two ions are 1.87 M and the solutions are not ideal. Consequently ΔH^0 only approximates the actual ΔH. Suppose nevertheless that dissolution of 15.0 g of ammonium nitrate in 100.0 g of pure water absorbs 5.26 kJ. This heat comes from the immediate surroundings of the dissolution reaction, which consist of 115.0 g of aqueous solution. The heat capacity of the immediate surroundings is close to 418 J K^{-1}, according to the problem. Their ΔT in furnishing the 5.26 kJ to the system is -12.6 K and their final T is 20.0 -12.6 = 7.4°C.
c) The dissolution of ammonium nitrate in water could be used in cold packs for first aid.

12.46 The combustion reaction is

$$C_6H_{10}(l) + \tfrac{17}{2}O_2(g) \rightarrow 6\,CO_2(g) + 5\,H_2O(l) \qquad \Delta H_{298}^0 = -3731.7 \text{ kJ}$$

Use Hess's law

$$-3731.7 \text{ kJ} = 6(-393.51) + 5(-285.83) - 1\left(\Delta H_f^0(C_6H_{10})(l)\right) - \tfrac{17}{2}(0)$$
$$\Delta H_f^0(C_6H_{12})(l) = -58.5 \text{ kJ mol}^{-1}$$

12.48 **a)** The combustion of benzoic acid: $C_6H_5COOH(s) + \frac{15}{2}O_2(g) \rightarrow 7\ CO_2(g) + 3\ H_2O(l)$.

b) The heat absorbed by the reaction is the negative of heat absorbed by the calorimeter.

$$\Delta U_{298}^0 = -q\text{v} = -C\Delta T = -(9.382 \text{ kJ K}^{-1}) \times (2.15 \text{ K}) = -20.17 \text{ kJ}$$

If 1.000 mol of benzoic acid burns:

$$\Delta U_{298}^0 = \left(\frac{-20.17 \text{ kJ}}{0.800 \text{ g}}\right) \times \left(\frac{122.12 \text{ g}}{\text{mol } C_6H_5COOH}\right)(1.000 \text{ mol } C_6H_5COOH) = -3.08 \times 10^3 \text{ kJ}$$

c) Use the relationship $\Delta H_{298}^0 = \Delta U_{298}^0 + \Delta n_g RT$ where Δn_g is the change in the number of moles of gas going from reactants to products:

$$\Delta H_{298}^0 = -3.08 \times 10^3 \text{ kJ} + \left(-\tfrac{1}{2} \text{ mol}\right)\left(0.008315 \text{ kJ K}^{-1}\text{mol}^{-1}\right)(298.15 \text{ K}) = -3.08 \times 10^3 \text{ kJ}$$

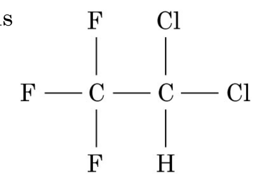
The difference between ΔH_{298}^0 and ΔU_{298}^0 is negligible.

d) Use Hess's law and the standard enthalpies of formation

$$-3080\text{ kJ} = 7\underbrace{(-393.51)}_{CO_2(g)} + 3\underbrace{(-285.83)}_{H_2O(l)} - 1\text{ mol}\left(\Delta H_f^0\left(C_6H_5COOH(s)\right)\right)$$

$$\Delta H_f^0\left(C_6H_5COOH(s)\right) = -532\text{ kJ mol}^{-1}$$

12.50 The structure of the compound is



It comes from its component elements in their standard states by

$$2\,C(s) + 3/2\,F_2(g) + 1/2\,H_2(g) + Cl_2(g) \rightarrow C_2F_3HCl_2(g)$$

In the following equation, each tabular value is multiplied by the number of moles of bonds formed (or number of moles of gaseous atoms formed by atomization).

$$\Delta H^0 = 2\underbrace{(716.7)\text{ kJ}}_{C(g)} + 3\underbrace{(79.0)\text{kJ}}_{F(g)} + 1\underbrace{(218.0)\text{kJ}}_{H(g)} + 2\underbrace{(121.7)\text{kJ}}_{Cl(g)} - 3\underbrace{(441)\text{kJ}}_{C\text{–}F}$$

$$-1\underbrace{(413)\text{kJ}}_{C\text{–}H} - 1\underbrace{(348)\text{kJ}}_{C\text{–}C} - 2\underbrace{(328)\text{kJ}}_{C\text{–}Cl} = -608\text{ kJ}$$

The molar ΔH_f^0 of $CF_3CHCl_2(g)$ is approximately -600 kJ mol^{-1}.

12.52 The reaction forming one mole of ethane from ethylene and hydrogen in their standard states can be imagined as breaking all the bonds in the reactants, which are one mole of gaseous ethylene and one mole of gaseous hydrogen, and then constructing one mole of ethane from the resulting gaseous atoms.

$$\Delta H^0 = 4\underbrace{(413)\text{kJ}}_{C\text{–}H} + 1\underbrace{(615)\text{kJ}}_{C=C} + 1\underbrace{(436)\text{kJ}}_{H\text{–}H} - 6\underbrace{(413)\text{kJ}}_{C\text{–}H} - 1\underbrace{(348)\text{kJ}}_{C\text{–}C} = -123\text{ kJ}$$

12.54 **a)** The left side of the equation, shows 6 moles of Hg—Cl bonds and 8 moles of Al—Cl bonds. The right side of the equation also shows 6 moles of Hg—Cl bonds and 8 moles of Al—Cl bonds (note that 2 mol of compound forms). The enthalpy of a single bond between two elements is nearly constant from compound to compound, so ΔH is close to zero.

b) The alternative structure of Hg_2Cl_4 contains 4 moles of Hg—CI bonds and 1 mole of Hg—Hg bonds. A ΔH differing significantly from zero would be expected because different bonds are broken than are formed.

12.56 Assume that the argon behaves ideally.

$$n_{\text{Ar}} = \frac{54.0 \text{ g}}{39.948 \text{ g mol}^{-1}} = 1.352 \text{ mol}$$

$$w = -nRT \ln\frac{P_1}{P_2} = -(1.352 \text{ mol})(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(400 \text{ K}) \ln\frac{1.50 \text{ atm}}{4.00 \text{ atm}} = +4410 \text{ J}$$

$$\Delta U = n_{\text{Ar}}\, c_{\text{V}}\Delta T = C_{\text{V}}(0) = 0$$

$$q = -w = -4410 \text{ J}$$

$$\Delta H = n_{\text{Ar}}\, c_{\text{P}}\Delta T = C_{\text{p}}(0) = 0$$

ΔU and ΔH do not equal zero in isothermal changes involving real gases because real gases have non-zero internal pressures $(\partial U/\partial V)_T$ as a consequence of attractions between their molecules.

12.58 For an adiabatic process, q = 0; for a reversible adiabatic compression of an ideal gas, $P_1V_1^{\gamma} = P_2V_2^{\gamma}$. First compute γ

$$\gamma = \frac{c_P}{c_V} = \frac{c_P}{c_P - R} = \frac{29.3 \text{ J K}^{-1}\text{mol}^{-1}}{(29.3 - 8.3145)\text{J K}^{-1}\text{mol}^{-1}} = 1.396$$

For this process, T_1 = 273.15 K, P_1 = 1.00 atm, and P_2 = 2.00 atm. Compute V_1 and T_2

$$V_1 = \frac{nRT_1}{P_1} = \frac{(2.00 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(273.15 \text{ K})}{1.00 \text{ atm}} = 44.83 \text{ L}$$

$$\left(\frac{V_2}{V_1}\right)^{\gamma} = \frac{P_1}{P_2} = 0.500 \quad \text{from which} \quad \frac{V_2}{V_1} = (0.500)^{1/\gamma} = 0.6087$$

$$V_2 = 0.6087(44.83 \text{ L}) = 27.29 \text{ L}$$

$$T_2 = \frac{P_2V_2}{nR} = \frac{(2.00 \text{ atm})(27.29 \text{ L})}{(2.00 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})} = 333 \text{ K}$$

$$\Delta U = nc_{\text{V}}\,\Delta T = (2.00 \text{ mol})(20.98 \text{ J K}^{-1}\text{mol}^{-1})(332.5 - 273.15 \text{ K}) = +2.5\times10^3 \text{ J}$$

$$w = \Delta U - q = \Delta U - 0 = 2.5\times10^3\text{J}$$

12.60 The problem is identical to problem **9.47** except that the separation of the two energy levels is 100 times larger

$$\frac{P_2}{P_1} = \frac{Ce^{-\epsilon_2/k_{\text{B}}T}}{Ce^{-\epsilon_1/k_{\text{B}}T}} = \frac{e^{-\epsilon_2/k_{\text{B}}T}}{e^{-\epsilon_1/k_{\text{B}}T}} = e^{-(\epsilon_2-\epsilon_1)/k_{\text{B}}T}$$

The energy difference and T are given in the problem, and the Boltzmann constant k_{B} is well-known. Insert the numbers

$$\frac{P_2}{P_1} = e^{-(40\times10^{-21}\text{ J})/1.38\times10^{-23}\text{ J K}^{-1}(298\text{ K})} = 6.0\times10^{-5}$$

12.62 Compute the energy difference between the vibrational levels and substitute it in the Boltzmann equation

$$\Delta \in = h\nu = \left(6.626\times10^{-34}\ \text{J s}\right)\left(1.15\times10^{13}\ \text{s}^{-1}\right) = 7.62\times10^{-21}\ \text{J}$$

$$\frac{P_2}{P_1} = \exp\left[\frac{-\Delta \in}{\kappa_B T}\right] = e^{-1.84} = 0.159$$

For every 1.00 × 10^6 molecules in the ground state (state 1), there are 0.159 × 10^6 = 1.59 × 10^5 molecules in the first excited state (state 2) at 300 K.

12.64 Compute μ_{HBr}, the reduced mass, and then ν_{HBr}, the fundamental vibrational frequency, of the HBr molecule:

$$\mu_{HBr} = \frac{m_{Br} m_H}{m_{Br} + m_H} = \frac{\left(79.904\ \text{u}\right)\left(1.008\ \text{u}\right)}{\left(79.904\ \text{u}\right)+\left(1.008\ \text{u}\right)} = 0.9954\ \text{u} = 1.653\times10^{-27}\ \text{kg}$$

$$\nu_{HBr} = \frac{1}{2\pi}\sqrt{\frac{\kappa_{HBr}}{\mu_{HBr}}} = \frac{1}{2\pi}\sqrt{\frac{412\ \text{N m}^{-1}}{1.653\times10^{-27}\text{kg}}} = 7.946\times10^{13}\ \text{s}^{-1}$$

The energy difference between the equally spaced vibrational levels of HF and the relative populations of the energy levels 1 and 0 at 300 K are respectively

$$\in_1 - \in_0 = h\nu = \left(6.626\times10^{-34}\ \text{J s}\right)\left(7.946\times10^{13}\ \text{s}^{-1}\right) = 5.265\times10^{-20}\ \text{J}$$

$$\frac{P_1}{P_0} = \exp\left(\frac{-\left(5.265\times10^{-20}\ \text{J}\right)}{\left(1.3808\times10^{-23}\ \text{J K}^{-1}\right)\left(300\ \text{K}\right)}\right) = e^{-12.71} = 3.02\times10^{-6}$$

12.66 The specific heat capacity of a substance in general changes with the temperature; the heat absorbed per unit mass of a substance in a temperature change at constant pressure is accordingly really an integral

$$q_P = \int_{T_1}^{T_2} c_s\, dT$$

The dependence of c_s on temperature is often slight, but in this problem it is large. Estimate the integral as the area under the curve in a plot of c_s versus T. The units of this area in this case are J g^{-1}. Estimate the area by adding up the areas of a series of columns of width 0.05 K and height equal to the average value of c_s at the two ends of each 0.05 K temperature range

$$0.05\ \text{K}\left(\frac{2.81+3.26}{2}+\frac{3.26+3.79}{2}+\frac{3.79+4.42}{2}+\frac{4.42+5.18}{2}\right.$$
$$\left.+\frac{5.18+6.16}{2}+\frac{6.16+7.51}{2}+\frac{7.51+9.35}{2}\right)\text{J K}^{-1}\ \text{g}^{-1} = 1.82\ \text{J}\ g^{-1}$$

At constant pressure, it requires about 1.82 J of heat to raise the temperature of 1.00 g of He(*l*) from 1.80 K to 2.15 K.

12.68

$$\Delta H = q_{\rm P} = \left[1.00 \text{ mol}\right]\left[38 \text{ J °C}^{-1} \text{ mol}^{-1}\left(0-\left(-30°\text{C}\right)\right)+\left(6007 \text{ J mol}^{-1}\right)\right.$$
$$\left.+75 \text{ J °C}^{-1}\text{mol}^{-1}\left(100-0°\text{C}\right)+40660 \text{ J mol}^{-1}+36 \text{ J °C}^{-1} \text{ mol}^{-1}\left(140-100°\text{C}\right)\right.$$
$$= 5.675\times10^{4}\text{ J} = 56.7 \text{ kJ}$$

$\Delta U = \Delta H - \Delta\left(PV\right) = \Delta H - \left(P_{\rm final}V_{\rm final} - P_{\rm initial}V_{\rm initial}\right) \approx \Delta H - P_{\rm final}V_{\rm final}$ because the volume of 1.00 mol of ice is very much less than the volume of 1.00 mol of steam.

$$P_{\rm final}V_{\rm final} = nRT = \left(1.00 \text{ mol}\right)\left(8.3145 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(413 \text{ K}\right) = 3.43\times10^{3}\text{ J}$$
$$\Delta U = 5.675\times10^{4} - 3.43\times10^{3} = 5.33\times10^{4}\text{ J}=53.3 \text{ kJ}$$
$$w = \Delta U - q = 53.3 - 56.7 = -3.4 \text{ kJ}$$

12.70 **a)** Substituting in $PV = nRT$ gives $P = 1.000$ atm.
b) $q = +3.000$ kJ.
c) The strong rigid container neither expands nor contracts during the heating. There is therefore no pressure-volume work. Because there is no other mechanical linkage (or electrical linkage) to the surroundings, $w = 0$.
d) The temperature change of the gas is given by

$$\Delta T = \frac{q}{n\,c_{\rm V}} = \frac{3000 \text{ J}}{\left(1.000 \text{ mol}\right)\left(12.47 \text{ J mol}^{-1}\text{K}^{-1}\right)} = 240.6 \text{ K}$$

so the final T is 513.7 K.
e) Use the ideal gas equation: $P = 1.881$ atm.
f) $\Delta U = q + w = 3000 + 0 = +3000$ J.
g) $\Delta H = \Delta U + \Delta\left(PV\right)$. Compute $\Delta\left(PV\right) = P_2V_2 - P_1V_1$. The result is 19.74 L atm, which is 2000 J. Hence, $\Delta H = 3000 + 2000 = +5000$ J.
h) The law of conservation of energy applies to energy, not enthalpy. The change in enthalpy is equal to the heat absorbed only if the pressure is held constant.

12.72 The energy released in the combustion of gasoline in fueling the car to travel a kilometer is

$$1 \text{ km}\times\left(\frac{1 \text{ L gasoline}}{8.0 \text{ km}}\right)\times\left(\frac{0.68 \text{ kg}}{1 \text{ L}}\right)\times\left(\frac{48\times10^{3}\text{kJ}}{1 \text{ kg}}\right) = 4080 \text{ kJ}$$

The energy released in the oxidation of food is about (100 / 0.3) kJ or 330 kJ. The energy savings is around 3800 kJ.

12.74

$$q_{\rm water} = \left(50.0 \text{ g}\right)\left(4.184 \text{ J K}^{-1} \text{ g}^{-1}\right)\left(23.36 - 25.00 \text{ K}\right) = -343 \text{ J}$$
$$\Delta H^{0} = \left(\frac{+343 \text{ J}}{1 \text{ g KClO}_3}\right)\left(\frac{122.55 \text{ g KClO}_3}{1 \text{ mol KClO}_3}\right) = +4.20\times10^{4} \text{ J} = +42.0 \text{ kJ}$$

12.76 The ΔH^{0} of the reaction is the difference between the $\Delta H_{\rm f}^{0}$'s of the products and the reactants. It is

$$2\underbrace{\left(96.23\right)}_{\rm HgBr(\mathit{g})} - 1\underbrace{\left(-206.77\right)}_{\rm Hg_2Br_2(\mathit{s})} = +399.2 \text{ kJ}$$

12.78

$$\Delta H_1 = (1\text{ mol})(39.9\text{ J K}^{-1}\text{mol}^{-1})(298-500\text{ K}) + (\tfrac{1}{2}\text{ mol})(29.4\text{ J K}^{-1}\text{mol}^{-1})(298-500\text{ K})$$
$$= -1.103\times10^{4}\text{ J}$$
$$\Delta H_2 = \Delta H^0_{298} = -395.72-(-296.83) = -98.89\text{ kJ}$$
$$\Delta H_3 = (1\text{ mol})(50.7\text{ J K}^{-1}\text{mol}^{-1})(500-298)\text{ K} = +1.024\times10^{4}\text{ J}$$
$$\Delta H^0_{500} = \Delta H_1+\Delta H_2+\Delta H_3 = -98.89-11.03+10.24\text{ kJ} = -99.7\text{ kJ}$$

The difference between ΔH^0_{500} and ΔH^0_{298} is slight, only about 0.8%.

12.80 Assume that the oxygen behaves ideally. Compute the chemical amount of O_2 and its heat capacity ratio

$$n_{O_2} = \frac{46.0\text{ g}}{32.00\text{ g mol}^{-1}} = 1.438\text{ mol O}_2 \qquad \gamma = \frac{c_P}{c_V} = \frac{29.4\text{ J K}^{-1}\text{mol}^{-1}}{(29.4-8.3145)\text{ J K}^{-1}\text{mol}^{-1}} = 1.394$$

Compute the volume before the reversible adiabatic expansion (V_1) and after (V_2)

$$V_1 = \frac{(1.438\text{ mol})(0.08206\text{ J K}^{-1}\text{mol}^{-1})(400\text{ K})}{1.00\text{ atm}} = 47.2\text{ L}$$

$$\left(\frac{V_2}{V_1}\right)^{\gamma} = \frac{P_1}{P_2} = \frac{1.00\text{ atm}}{0.60\text{ atm}} = 1.667 \qquad \frac{V_2}{V_1} = (1.667)^{1/\gamma} = 1.442 \qquad V_2 = 1.442\ V_1 = 68.1\text{ L}$$

The temperature after the adiabatic expansion is

$$T_2 = \frac{(0.60\text{ atm})(68.1\text{ L})}{(1.4375\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})} = 346\text{ K} \approx 350\text{ K}$$

Determine the change in the internal energy and the work absorbed during the adiabatic expansion

$$\Delta U_{\text{exp}} = nc_V\Delta T = (1.438\text{ mol})(29.4-8.3145\text{ J K}^{-1}\text{mol}^{-1})(346-400)\text{ K} = -1640\text{ J}$$

$$w_{\text{exp}} = \Delta U_{\text{exp}} - q_{\text{exp}} = -1640\text{ J} - 0\text{ J} = -1640\text{ J}$$

In the isothermal compression V decreases at constant T from 68.1 back to 47.2 L,

$$P_{\text{final}} = \frac{68.1\text{ L}}{47.2\text{ L}}\times 0.60\text{ atm} = 0.87\text{ atm}$$

The internal energy of the gas remains constant during this change because the gas is ideal. $\Delta U_{\text{comp}} = 0$. Compute the work during the reversible compression using the standard formula

$$w_{\text{comp}} = -nRT\ \ln\left(\frac{47.2\text{ L}}{68.1\text{ L}}\right) = +1.52\times10^{3}\text{ J}$$
$$q_{\text{comp}} = \Delta U_{\text{comp}} - w_{\text{comp}} = 0\text{ J} - 1.52\times10^{3}\text{ J} = -1.52\times10^{3}\text{ J}$$

For the overall change

$$\Delta U_{\text{overall}} = \Delta U_{\text{exp}} + \Delta U_{\text{comp}} = -1640\text{ J} + 0\text{ J} = -1640\text{ J}$$
$$w_{\text{overall}} = w_{\text{exp}} + w_{\text{comp}} = -1640\text{ J} + 1520\text{ J} = -120\text{ J}$$
$$q_{\text{overall}} = q_{\text{exp}} + q_{\text{comp}} = 0\text{ J} - 1520\text{ J} = -1520\text{ J}$$

12.82 **a)** $\Delta H^0 = 2(-393.51) + 3(-241.82) - 2(-112) = -1288$ kJ. This is for the reaction as written, which is for the burning of 2 mol. For 1 mol, ΔH^0 would be -644 kJ. The reaction is highly exothermic.

b) If $CH_3NO_2(g)$ were burned the reaction would be more exothermic by the molar heat of vaporization of nitromethane, *i.e.* the gas has a higher enthalpy than $CH_3NO_2(l)$. Formally, ΔH^0 for the reaction $CH_3NO_2(g) \rightarrow CH_3NO_2(l)$ (a negative number) is added to ΔH^0 for burning 1 mol of $CH_3NO_2(l)$.

12.84 The problem concerns isobutene, not isobutane, as stated in some printings of the text.

a) $C_4H_8(g) + 6\ O_2(g) \rightarrow 4\ CO_2(g) + 4\ H_2O(g)$.

The standard enthalpy of formation of isobutene ΔH_f^0 is related to ΔH^0 of this reaction by

$-2528\text{ kJ} = 4(-393.51\text{ kJ}) + 4(-241.82\text{ kJ}) - \Delta H_f^0$ from which $\Delta H_f^0 = -13\text{ kJ mol}^{-1}$

b) When 0.50 mol of isobutene is burned at constant pressure

$$q_P = 0.50(-2528)\text{ kJ} = -1.3\times10^3\text{ kJ}$$

If this is done adiabatically, then the heat will be absorbed by the substances present at the conclusion of the reaction and by the reaction vessel; their temperature will rise. The products consist of 2 mol CO_2, 2 mol H_2O, and 5 mol O_2. The heat capacity of this mixture and the calorimetry assembly is

$$C_P = ((2\times37) + (2\times34) + (5\times29) + (700))\text{ J K}^{-1} = 987\text{ J K}^{-1}$$

The temperature rise will be about 1.3×10^6 J/987 J K^{-1} = 1.3×10^3 K. Since the initial temperature was near to 300 K, the final temperature is near to 1600 K, or about 1300°C.

12.86 The reaction is

$$ClF_3(g) + 4\ Li(s) \rightarrow LiCl(s) + 3\ LiF(s)$$

and the amounts are 0.3472 mol ClF_3 and 2.492 mol Li. The limiting reactant is ClF_3. If one mole of ClF_3 reacted,

$$\Delta H^0 = -408.61 + 3(-615.97) - (-163.2) = -2093.3\text{ kJ}$$

The ΔH for 0.3472 mol reacting is smaller by a factor of 0.3472, giving ΔH = -727 kJ. The amount of heat *evolved* is 727 kJ.

12.88 **a)** The point of drawing all the Lewis structures is to identify the type and number of bonds in the compounds in parts **b)** through **d)**. The O_2 has an O=O double bond; CO_2 has two C=O double bonds; H—O—H has two O—H single bonds; CH4 has four C—H single bonds, C_2H_5OH has five C—H single bonds, one C—C single bond, one C—O single bond, and one O—H single bond; C_8H_{18} has 18 C—H single bonds and seven C—C single bonds,

b) For the burning of one mole of methane

$$\Delta H^0 = -\underbrace{4(463)}_{4\text{ O–H}} - \underbrace{2(728)}_{2\text{ C=O}} + \underbrace{4(413)}_{4\text{ C–H}} + \underbrace{2(498)}_{2\text{ O=O}} = -660\text{ kJ}$$

c) For the burning of one mole of octane

$$\Delta H^0 = -\underbrace{18(463)}_{18\ \text{O–H}} - \underbrace{16(728)}_{16\ \text{C=O}} + \underbrace{18(413)}_{18\ \text{C–H}} + \underbrace{7(348)}_{7\text{C–C}} + \underbrace{25/2(498)}_{25/2\ \text{O=O}} = -3887\ \text{kJ}$$

d) For the burning of one mole of ethanol

$$\Delta H^0 = -\underbrace{6(463)}_{6\ \text{O–H}} - \underbrace{4(728)}_{4\ \text{C=O}} + \underbrace{5(413)}_{5\ \text{C–H}} + \underbrace{1(348)}_{1\ \text{C–C}} + \underbrace{1(351)}_{1\ \text{C–O}} + \underbrace{1(463)}_{1\ \text{O–H}} + \underbrace{3(498)}_{3\ \text{O=O}} = -969\ \text{kJ}$$

12.90 **a)** Before the expansion, the average velocity is zero, and the average speed is

$$\bar{u} = \sqrt{\frac{8\,RT}{\pi\mathcal{M}}} = \sqrt{\frac{8(8.3145\ \text{J mol}^{-1}\text{K}^{-1})(400\ \text{K})}{\pi(0.0040\ \text{kg mol}^{-1})}} = 1.46\times10^{3}\ \text{m s}^{-1}$$

b) Treat helium as a monatomic ideal gas. Then $\gamma = \frac{5}{3}$. Assume that the expansion through the nozzle is reversible and adiabatic. Then use the equations relating *P, V, T* that appear in text Section 12.6

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{V_1^{\gamma}}{V_2^{\gamma}}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{P_2}{P_1}\right)^{2/5}$$

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{2/5} = 400\ \text{K}\left(\frac{1.0\ \text{atm}}{50\ \text{atm}}\right)^{2/5} = 84\ \text{K}$$

c) The temperature of the helium after the expansion is only 84 K. The average speed of the atoms of the gas in their random thermal motions has fallen to

$$\bar{u} = \sqrt{\frac{8\,RT}{\pi\mathcal{M}}} = \sqrt{\frac{8(8.3145\ \text{J mol}^{-1}\text{K}^{-1})(84\ \text{K})}{\pi(0.0040\ \text{kg mol}^{-1})}} = 667\ \text{m s}^{-1}$$

The change in random thermal energy per mole of He that goes through the nozzle is

$$\Delta E = \tfrac{3}{2}RT_f - \tfrac{3}{2}RT_i = \tfrac{3}{2}(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\times(84-400\ \text{K}) = -3941\ \text{J mol}^{-1}$$

This energy appears as kinetic energy of *directed* motion of the expelled helium. This macroscopic, non-thermal kinetic energy belongs to the whole parcel of helium as it travels away from the nozzle. The velocity of the parcel and therefore the average velocity of the molecules that compose it is

$$\bar{v}\ (\text{directed}) = \sqrt{\frac{2(-\Delta E)}{\mathcal{M}}} = \sqrt{\frac{2(+3941\ \text{J mol}^{-1})}{0.0040\ \text{kg mol}^{-1}}} = 1400\ \text{m s}^{-1}$$

The motion of the expelled helium is indeed supersonic. The speed of sound in dry air at room conditions is only about 350 m s^{-1}.

Chapter 13

Spontaneous Processes and Thermodynamic Equilibrium

13.2 All five processes occur in the real world and thus are spontaneous.
a) *System*: HCl and NaOH solutions; *surroundings*: container, buret, air; *constraint removed*: opening the stopcock of the buret removes the initial constraint that the two solutions are separated.
b) *System*: Zn(*s*) and HCl(*aq*); *surroundings*: container, air; *constraint removed*: The imaginary barrier between the zinc and the HCl solution is removed, allowing zinc ions and gaseous hydrogen to form.
c) *System*: rubber band; *surroundings*: weight, air; *constraint removed*: the length of the rubber band becomes unconstrained.
d) *System*: gas; *surroundings*: chamber, piston; *constraint removed*: The volume of the gas in the chamber becomes unconstrained.
e) *System*: Water (ice); *surroundings*: refrigerator; *constraint removed*: thermal barrier separating the water in the tray from its surroundings.

13.4 **a)** Label the three equal volumes *L* (left), *C* (center), and *R* (right). Each of the four molecules could be in any one of the three; each has three equally probable ways of going into the overall volume. The number of microstates is therefore 3^4 or 81.
b) In only 1 of the 81 microstates are all four molecules in *L*. Thus the probability is 1/81.

13.6 A system containing the "chemically mixed" boron halides has greater entropy than a system of just BCl_3 and BF_3. It has the same number of gas-phase molecules, but more distinguishable kinds of molecules, hence more microstates and higher entropy.

13.8

Chance that all N_2 is in left half = $\left(\frac{1}{2}\right)^{2N_A}$ Chance that all O_2 is in right half = $\left(\frac{1}{2}\right)^{N_A}$

$$\text{Joint probability} = \left(\frac{1}{2}\right)^{2N_A}\left(\frac{1}{2}\right)^{N_A} = \left(\frac{1}{2}\right)^{3N_A} = \left(\frac{1}{2}\right)^{1.81\times10^{24}} = \frac{1}{10^{5.4\times10^{23}}}$$

13.10 a) Computer constructed: $\Delta S < 0$. **b)** Gas leaks out: $\Delta S > 0$. **c)** Solid sublimes: $\Delta S > 0$.

13.12 The melting point of tetraphenylgermane is 505.65 K.

$$\Delta H_{\text{fus}} = 381.03 \text{ g mol}^{-1} \times 106.7 \text{ J g}^{-1} = 4.066 \times 10^4 \text{ J mol}^{-1}$$

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} = \frac{4.066 \times 10^4 \text{ J mol}^{-1}}{505.65 \text{ K}} = 80.40 \text{ J K}^{-1}\text{mol}^{-1}$$

These are the values at the melting point (232.5°C), not at 25°C.

13.14 Trouton's rule states that the molar entropy of vaporization of most substances approximates 88 J $K^{-1}mol^{-1}$. Gas and liquid forms of a substance are in equilibrium at the normal boiling point, so

$$T_{\text{b}} = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{16.15 \times 10^3 \text{ J mol}^{-1}}{88 \text{ J K}^{-1}\text{mol}^{-1}} = 184 \text{ K}$$

13.16 The chemical amount of HBr in the system is 60.0 g/80.91 g mol^{-1} = 0.7415 mol; the heat capacity of HBr(g) at constant volume is $c_V = c_P - R = 29.1 - 8.3 = 20.8 \text{ J K}^{-1}\text{mol}^{-1}$. Designate the reversible isochoric heating as step 1 and the isothermal reversible expansion as step 2. Compute all of the quantities separately for the two steps and add them up.

$$w_1 = 0 \left(\text{no } P\text{-}V \text{ work is possible at constant volume}\right)$$

$$q_1 = q_V = nc_V\ \Delta T = \left(0.7415 \text{ mol}\right)\left(20.8 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(500 - 300 \text{ K}\right) = 3085 \text{ J}$$

$$\Delta U_1 = nc_V\ \Delta T = 3085 \text{ J}$$

$$\Delta H_1 = nc_P\ \Delta T = \left(0.7415\right)\left(29.1 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(500 - 300 \text{ K}\right) = 4316 \text{ J}$$

$$\Delta S_1 = nc_V\ \ln \frac{T_{\text{f}}}{T_{\text{i}}} = \left(0.7415\right)\left(20.8 \text{ J K}^{-1}\text{mol}^{-1}\right)\ln\frac{500 \text{ K}}{300 \text{ K}} = 7.88 \text{ J K}^{-1}$$

The heating in step 1 raises the pressure of the system by the factor 500 K/300 K = 5/3. The expansion in step 2 takes place at a constant temperature of 500 K and lowers the pressure by this same factor. Because the gas is ideal the volume must increase in step 2 by the factor 5/3

$$q_2 = nRT\ \ln\frac{V_{\text{f}}}{V_{\text{i}}} = \left(0.7415 \text{ mol}\right)\left(8.3145 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(500 \text{ K}\right)\ln\frac{5}{3} = 1575 \text{ J}$$

$$\Delta U_2 = 0\ \left(\text{an isothermal process on an ideal gas}\right)$$

$$\Delta H_2 = 0\ \left(\text{an isothermal process on an ideal gas}\right)$$

$$w_2 = -1575 \text{ J}\ \left(\text{by the first law}\right)$$

$$\Delta S_2 = \frac{q_2}{T} = \frac{1575 \text{ J}}{500 \text{ K}} = 3.15 \text{ J K}^{-1}$$

The totals for the two steps are

$$\Delta U = \Delta U_1 + \Delta U_2 = 3085\text{ J} + 0\text{ J} = 3085\text{ J} = 3.08\text{ kJ}$$
$$q = q_1 + q_2 = 3085\text{ J} + 1575\text{ J} = 4660\text{ J} = 4.66\text{ kJ}$$
$$w = w_1 + w_2 = 0\text{ J} + (-1575\text{ J}) = -1575\text{ J} = -1.58\text{ kJ}$$
$$\Delta H = \Delta H_1 + \Delta H_2 = 4316\text{ J} + 0\text{ J} = 4316\text{ J} = 4.32\text{ kJ}$$
$$\Delta S = \Delta S_1 + \Delta S_2 = 7.88\text{ J K}^{-1} + 3.15\text{ J K}^{-1} = 11.0\text{ J K}^{-1}$$

13.18 Imagine the *reversible* heating of 1.00 mol of water from 25°C to 150°C. in these three steps: heating the water to 100°C, evaporating the water to steam at 100°C, heating the steam from 100°C to 150°C. Then

$$q = (1.00\text{ mol})(75.4\text{ J K}^{-1}\text{mol}^{-1})(100-25\text{ K}) + (1.00\text{ mol})(40680\text{ J K}^{-1}\text{mol}^{-1})$$
$$+ (1.00\text{ mol})(36.0\text{ J K}^{-1}\text{mol}^{-1})(150-100\text{ K}) = 48135\text{ J} = 48.13\text{ kJ}$$

The change in the entropy of the 1.00 mol of water in the process is

$$\Delta S_{\text{water}} = nc_P(l)\ln\frac{T_b}{T_i} + n\frac{\Delta H_{\text{vap}}}{T_b} + nc_P(g)\ln\frac{T_f}{T_b}$$
$$= (1.00\text{ mol})(75.4\text{ J K}^{-1}\text{mol}^{-1})\ln\frac{373.15}{298.15} + (1.00\text{ mol})\frac{40680\text{ J mol}^{-1}}{373.15\text{ K}}$$
$$+ (1.00\text{ mol})(36.0\text{ J K}^{-1}\text{mol}^{-1})\ln\frac{423.15}{373.15} = 130\text{ J K}^{-1}$$

Now consider the flash evaporation, an irreversible process. Because S is a function of state, ΔS_{water} is still 130 J K^{-1}, but things are different for the iron. The iron loses 48 135 J of heat at a constant temperature of 150°C (423.15 K). The final state of the iron is identical to the state that would be achieved by removing 48 135 J reversibly at 423.15 K. Accordingly $\Delta S_{\text{iron}} = q/T = -48\,135\text{ J}/423.15\text{ K} = -113.8\text{ J K}^{-1}$.

$$\Delta S_{\text{total}} = \Delta S_{\text{Fe}} + \Delta S_{\text{water}} = 130.5\text{ J K}^{-1} - 113.8\text{ J K}^{-1} = 17\text{ J K}^{-1} = 17\text{ J K}^{-1}$$

13.20 **a)**

$$\Delta H_{\text{Fe}} = nc_P\Delta T = (1.00\text{ mol})(25.1\text{ J K}^{-1}\text{mol}^{-1})(273.15-373.15\text{ K}) = -2510\text{ J} = -2.51\times10^3\text{ J}$$
$$\Delta S_{\text{Fe}} = nc_P\ln\frac{T_f}{T_i} = (1.00\text{ mol})(25.1\text{ J K}^{-1}\text{mol}^{-1})\ln\frac{273.15}{373.15} = -7.83\text{ J K}^{-1}$$

b) The entropy S is a function of state, and the initial and final states of the piece of iron are the same as in part **a)**. Therefore $\Delta S_{\text{Fe}} = -7.83\text{ J K}^{-1}$. The reservoir of water gains the 2510 J of heat from the piece of iron at a constant temperature of 273.15 K. Therefore $\Delta S_{\text{water}} = 2510\text{ J}/273.15\text{ K} = +9.19\text{ J K}^{-1}$.

$$\Delta S_{\text{total}} = \Delta S_{\text{Fe}} + \Delta S_{\text{water}} = 1.36\text{ J K}^{-1}$$

13.22 **a)** For the reaction as written in the problem

$$\Delta S^0_{298} = 1\underbrace{(130.57)}_{H_2(g)} + 1\underbrace{(213.63)}_{CO_2(g)} + 1\underbrace{(243.30)}_{CH_3NH_2(g)} - 1\underbrace{(282.4)}_{CH_3COOH(g)} - 1\underbrace{(192.34)}_{NH_3(g)} = +112.8 \text{ J K}^{-1}$$

where the numbers in parenthesis are standard molar entropies at 25° (with units of J K^{-1} mol^{-1}) and the other numbers are the coefficients (in moles) in the balanced equation.

b) It is a certainty that the suggested new reactants, which comprise a mole of a solid and a mole of a liquid, have less entropy than the two moles of gaseous reactants in the equation in part a). The products have the same entropy so the change in entropy is larger than in part **a)**.

13.24 Compute the standard entropies of formation at 298 K of the four hydrogen halides using the data in text Appendix D:

$$\Delta S^0_f(\text{HX}(g)) = 2\ S^0(\text{HX}(g)) - S^0(\text{X}_2(g)) - S^0(\text{H}_2(g))$$

$$\Delta S^0_f(\text{HF}(g)) = 2\underbrace{(173.67)}_{HF(g)} - \underbrace{(202.67)}_{F_2(g)} - \underbrace{(130.57)}_{H_2(g)} = 14.10 \text{ J K}^{-1}$$

$$\Delta S^0_f(\text{HCl}(g)) = 2\underbrace{(186.80)}_{HCl(g)} - \underbrace{(222.96)}_{Cl_2(g)} - \underbrace{(130.57)}_{H_2(g)} = 20.07 \text{ J K}^{-1}$$

$$\Delta S^0_f(\text{HBr}(g)) = 2\underbrace{(198.59)}_{HBr(g)} - \underbrace{(245.35)}_{Br_2(g)} - \underbrace{(130.57)}_{H_2(g)} = 21.26 \text{ J K}^{-1}$$

$$\Delta S^0_f(\text{HI}(g)) = 2\underbrace{(206.48)}_{HI(g)} - \underbrace{(260.58)}_{I_2(g)} - \underbrace{(130.57)}_{H_2(g)} = 21.81 \text{ J K}^{-1}$$

Although ΔS^0_f gets uniformly larger going down the periodic table, the value for HF(*g*) is much smaller than a trend-line based on the other three values predicts.

13.26 The fundamental criterion for spontaneity in any process is the sign of ΔS_{univ}, and

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

The positive ΔS^o quoted for the decomposition of quartz is a ΔS_{sys}. At room conditions ΔS_{surr} for the decomposition is even larger in magnitude and negative in sign. The surroundings have to supply a large amount of heat to the system to break the strong Si—O bonds in quartz. The temperature of the surroundings is too low for this to happen without a prohibitive decrease in their entropy.

13.28 **a)** The solvent, water, becomes ordered around the dissolved ions, which reduces its entropy. This must more than compensate for the increased entropy of the ions themselves.

b) $\Delta S^0 = -53.1 + 2(-13.8) - 68.87 = -149.6 \text{ J K}^{-1}$. Fluoride ions form hydrogen bonds with water, which lowers the entropy of the products still further.

13.30 **a)** At constant temperature and pressure $\Delta G = \Delta H - T\Delta S.$ Substitution then gives

$$\Delta G = -2.1\times10^{3}\ \text{J} - \left(243.15\ \text{K}\right)\left(-7.4\ \text{J K}^{-1}\right) = -301\ \text{J} = -3.0\times10^{3}\ \text{J}$$

It is assumed that the ΔH and $\Delta S,$ which change with temperature, are approximately correct at 243.15 K.

b) If the amount of tin is increased from 1.00 mol to 2.50 mol, then the ΔG increases by the same factor of 2.50, from -300 to -750 J, because of the larger size of the system.

c) The ΔG of the process at -30°C is negative, so white tin (in any amount) tends to convert spontaneously to gray tin at this low temperature.

d) At equilibrium at constant temperature and pressure, $\Delta G = 0.$ Compute the temperature that makes this condition happen:

$$T = \frac{\Delta H}{\Delta S} = \frac{-2.1\times10^{3}\text{J}}{-7.4\ \text{J K}^{-1}} = 284\ \text{K} = 2.8\times10^{2}\ \text{K}$$

13.32 Imagine three steps: (1) cooling superheated ice from 25°C to 0°C, (2) melting the cooled ice to water at 0°C; and (3) warming the liquid water to 25° C. Then

$$\begin{aligned}\Delta H &= \Delta H_{1} + \Delta H_{2} + \Delta H_{3}\\ &= nc_{P}\left(s\right)\left(0-25\right) + 6007\ \text{J} + nc_{P}\left(l\right)\left(25-0\right) = 6007\ \text{J}\end{aligned}$$

because $c_P(s) = c_P(l)$ by assumption. Similarly,

$$\Delta S = \Delta S_{1} + \Delta S_{2} + \Delta S_{3} = \Delta S_{2} = \frac{6007\ \text{J}}{273.15\ \text{K}} = 21.99\ \text{J K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = 6007\ \text{J} - \left(21.99\ \text{J K}^{-1}\right)\left(298.15\ \text{K}\right) = -550\ \text{J}$$

13.34 The mode of coupling between the oxidation of glucose and the reduction of ADP^{-3} is not explained. Fortunately, it is not necessary to know it. Simply combine the free energy changes of the two reactions by adding 38 times the first to the second

$$\Delta G_{\text{tot}} = -2872 + 38\left(34.5\right) = -1561\ \text{kJ}$$

Because $\Delta G < 0,$ the coupled process is spontaneous. The fraction of free energy stored is

$$\frac{38\left(34.5\ \text{kJ}\right)}{2872\ \text{kJ}} = 0.456$$

13.36 **a)** For $CO\left(g\right) + Cl_{2}\left(g\right) \rightarrow COCl_{2}\left(g\right),\ \Delta H^{0}_{298} = -108.3\ \text{kJ}$ and $\Delta S^{0}_{298} = -136.99\ \text{J K}^{-1}.$ If $\Delta G = 0,$ then

$$T = \frac{\Delta H^{0}_{298}}{\Delta S^{0}_{298}} = \frac{-108.3\ \text{kJ}}{-136.99\ \text{J K}^{-1}} = 790\ \text{K}$$

Below this temperature the reaction is spontaneous. The assumption (see problem **13.37**) that ΔH^{0}_{790} and ΔS^{0}_{790} equal ΔH^{0}_{298} and ΔS^{0}_{298} respectively is weak enough that only two significant figures seem justified.

b) For $2\ KClO_{3}\left(s\right) \rightarrow KCl\left(s\right) + 3O_{2}\left(g\right),\ \Delta H^{0}_{298} = -78.04\ \text{kJ};\ \Delta S^{0}_{298} = 494.1\ \text{J K}^{-1}.$ The reaction is spontaneous at all temperatures.

c) For $FeO(s) + C(s) \rightarrow Fe(s) + CO(g)$, use the Appendix D values tabulated for graphite (not diamond) and for wüstite. Then, $\Delta H^0_{298} = 155.75 \text{ kJ}$, and $\Delta S^0_{298} = 161.61 \text{ J K}^{-1}$. The reaction is spontaneous above about 960 K.

13.38 **a)** $\Delta G^0_{298} = 2\underbrace{(0)}_{W(s)} + 3\underbrace{(-394.36)}_{CO_2(g)} - 3\underbrace{(0)}_{C(s)} - 2\underbrace{(-764.08)}_{WO_3(s)} = +345.08 \text{ kJ}.$

The process is infeasible at room temperature because the reaction is *not* spontaneous at 298 K.
b) Raise the temperature. The fact that a gas is generated from solids means that ΔS for this reaction is positive. A high enough temperature will make ΔG negative no matter what the value of ΔH.

13.40 **a)**

$$\in = \frac{T_h - T_l}{T_h} = \frac{(400 - 300) \text{ K}}{400 \text{ K}} = 0.25$$

b)

$$0.25 = \frac{q_h + q_l}{q_h} = \frac{(1000 + q_l) \text{ J}}{1000 \text{ J}} \quad \text{hence} \quad q_l = (250 - 1000) \text{ J} = -750 \text{ J}$$

c)

$$\in = \frac{-w_{\text{net}}}{q_h} = \frac{-w_{\text{net}}}{1000 \text{ J}} = 0.250$$

$$-w_{\text{net}} = 250 \text{ J} = \text{maximum work performed } by \text{ engine}$$

13.42 Let the system consist of the mixed ice and water in the container. The container is thermally insulated so $q = 0$. The container is rigid, which excludes PV work and no other linkage exists to convey work to or from the surroundings. Hence $w = 0$. By the first law, $\Delta U = 0$. The internal energy of the system remains constant during the process.
At equilibrium the hot water will have cooled and some or all of the ice will have melted spontaneously. The change occurs in isolation from the surroundings so $\Delta S_{\text{surr}} = 0$. The second law states that for this spontaneous process $\Delta S_{\text{univ}} > 0$. Hence $\Delta S_{\text{sys}} > 0$.

13.44 The easy way to calculate ΔS_{sys} is to imagine a direct path from the overall initial state to the overall final state. This change is achieved by constant pressure heating, so

$$\Delta S_{\text{sys}} = nc_P \ln\frac{T_2}{T_1} = (1.00 \text{ mol}) \times \tfrac{5}{2}(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \ln\frac{400}{300} = 5.98 \text{ J K}^{-1}$$

The same answer comes, with much more effort, by adding ΔS_{sys} for the four steps given.

13.46 The mixing takes place in a thermally insulated vessel so that there is no heat exchange with the environment; the entropy of the environment does not change. The system (the 81.0 g of water) increases in entropy because the process is irreversible. Figure the final temperature of the system. Because $q_{\text{sys}} = 0$,

$$54.0 \text{ g}(4.18 \text{ J K}^{-1}g^{-1})(t_f - 0°\text{C}) + 27.0 \text{ g}(4.18 \text{ J K}^{-1}\text{g}^{-1})(t_f - 100°\text{C}) = 0$$

$$t_f = 33.3°\text{C}$$

View the heat transfer during the mixing as the combination of two reversible steps

Step 1 54.0 g $H_2O(l)$ at 0°C → 54.0 g $H_2O(l)$ at 33.3°C

Step 2 27.0 g $H_2O(l)$ at 100°C → 27.0 g $H_20(l)$ at 33.3°C

Figure the entropy changes of the two steps and add them

$$\Delta S_1 = m_1 c_V \ln\frac{T_f}{T_i} = (54.0 \text{ g})(4.18 \text{ J K}^{-1} \text{ g}^{-1}) \ln\frac{(273.15+33.33) \text{ K}}{(273.15+0)\text{K}} = 26.0 \text{ J K}^{-1}$$

$$\Delta S_2 = m_2 c_V \ln\frac{T_f}{T_i} = (27.0 \text{ g})(4.18 \text{ J K}^{-1} \text{ g}^{-1}) \ln\frac{(273.15+33.33) \text{ K}}{(273.15+100)\text{K}} = -22.2 \text{ J K}^{-1}$$

$$\Delta S_{sys} = \Delta S_1 + \Delta S_2 = 3.8 \text{ J K}^{-1}$$

13.48 The chance that the first of the 500 atoms sits in the left half of the optical trap is 1/2. Assume that the gas of sodium atoms behaves ideally. Then the chance that a second sodium atom joins the first in the left half of the optical trap is not influenced by the presence of the first and is also 1/2. The chance that both atoms are in the left half is 1/2 × 1/2 = 1/4. By extension, *p,* the chance that all 500 sodium atoms are in the left half, is

$$p = \left(\frac{1}{2}\right)^{500}$$

To compute p take the logarithm of both sides of the equation

$$\log p = 500 \log\frac{1}{2} = 500 \times (-0.30103) = -150.51$$

and then the antilog of both sides

$$p = 10^{-150.51} = 10^{0.49} \times 10^{-151} = 3 \times 10^{-151}$$

Even with this very small sample of gas, the chance of "spontaneous congregation" on one side of the vessel is essentially zero.

13.50 **a)** The random crystal has 2^{N_A} microstates or $10^{1.81\times10^{23}}$ microstates.
b) Let state 2 of the crystal be the ordered state and state 1 the random state. State 2 has just 1 microstate, but state 1 has many (as just computed).

$$\begin{aligned}\Delta S &= S_2 - S_1 \\ &= \kappa_B(\ln \Omega_2 - \ln \Omega_1) = \kappa_B \ln\frac{\Omega_2}{\Omega_1} \\ &= (1.38\times10^{-23} \text{ J K}^{-1}) \ln\frac{1}{10^{1.81\times10^{23}}} \\ &= (1.38\times10^{-23} \text{ J K}^{-1})((-1.81\times10^{23})\ln 10) = -5.76 \text{ J K}^{-1}\end{aligned}$$

13.52 **a)** The process takes 2.00 mol of an ideal monatomic gas from V = 19.15 L to 38.30 L and from T = 350 K to 272 K. To calculate ΔS_{sys} connect the same two states by a reversible path. Let the gas first expand reversibly at constant temperature

$$\Delta S_1 = nR \ln\frac{V_2}{V_1} = (2.00 \text{ mol})(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \ln\frac{38.50 \text{ L}}{19.15 \text{ L}} = 11.5 \text{ J K}^{-1}$$

and then cool reversibly at constant volume:

$$\Delta S_2 = nc_V \ln\frac{T_2}{T_1} = (2.00 \text{ mol})\left(\tfrac{3}{2}\right)(8.3145 \text{ J K}^{-1}\text{mol}^{-1})\ln\frac{272 \text{ K}}{350 \text{ K}} = -6.3 \text{ J K}^{-1}$$

Thus $\Delta S_{sys} = \Delta S_1 + \Delta S_2 = 5.2 \text{ J K}^{-1}$. Because $q = 0$, $\Delta S_{surr} = 0$, and $\Delta S_{univ} = 5.2 \text{ J K}^{-1}$.

b)

$$\Delta G_{sys} = \Delta H_{sys} - \Delta(TS)\text{sys} = nc_P\Delta T - (T_2S_2 - T_1S_1)$$

$$= (2.00 \text{ mol})\left(\tfrac{5}{2}\right)(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(272 - 350 \text{ K})$$

$$-(272 \text{ K})(158.2 + 5.2 \text{ J K}^{-1}) + (350 \text{ K})(158.2 \text{ J K}^{-1})$$

$$= -3\,243 \text{ J} - 44\,445 \text{ J} + 55\,370 \text{ J} = +7\,680 \text{ J} = 7.7\times \text{ kJ}$$

Note that ΔG_{sys} exceeds zero even though this process is spontaneous. $\Delta G_{sys} < 0$ is a criterion for spontaneity only at constant temperature and pressure. $\Delta S_{univ} > 0$ is the only completely general criterion.

13.54 At equilibrium between solid and gaseous iodine:

$$\Delta G = 0 = \Delta H - T\Delta S$$

so that $T = \Delta H/\Delta S$. Approximate the ΔH and ΔS of the process at the sublimation temperature by ΔH^0_{298} and ΔS^0_{298}. Compute these two quantities for the reaction $I_2(s) \rightleftharpoons I_2(g)$ in the usual way using the data in Appendix D. Then

$$T = \frac{62.44\times 10^3 \text{ J}}{144.44 \text{ J K}^{-1}} = 432.3 \text{ K}$$

The computation indicates that solid iodine and gaseous iodine are in equilibrium at 159.1°C when the pressure of the gaseous iodine is 1 atm. The melting point of $I_2(s)$ is 113.5°C at $P = 1$ atm (from Appendix F). The solid-gas equilibrium at 1 atm cannot be accomplished because the solid melts first. Solid iodine ordinarily sublimes at room conditions (a well-known fact) because the partial pressure of gaseous iodine in ordinary rooms is much less than 1 atm.

13.56 A is the more stable phase, at least under standard conditions, since it has the lower standard free energy. It follows that A under these conditions has the lower vapor pressure and the lower solubility.

13.58 Dissociation of any substance with diatomic molecules has a positive ΔH and a positive ΔS. This combination of signs means that a temperature exists above which ΔG of dissociation is negative, and the substance tends to dissociate into its constituent atoms. That temperature T is given by $T = \Delta H/\Delta S$. For CO*(g),*

$$T = \frac{1.05\times 10^3 \text{ kJ}}{0.11 \text{ kJ K}^{-1}} = 9.5\times 10^3 \text{ K}$$

If the most stable diatomic molecules tend to dissociate above 9 500 K, then all molecules tend to dissociate above 9 500 K: no molecules; no chemistry of molecules. Note that the ΔS of this reaction is pressure-dependent. It increases by $R \ln 10 = 19 \text{ J K}^{-1}$ (in accord with text equation 13.9) for each 10-fold decrease in pressure. At pressures much lower than 1 atm, ΔS is even larger and the maximum temperature for stability is lower.

13.60 The formation reactions for the two compounds are quite similar.

$$\text{Pt}(s) + \text{N}_2(g) + 3\ \text{H}_2(g) + \text{I}_2(s) \rightleftharpoons \textit{cis}\text{-Pt}(\text{NH}_3)_2\text{I}_2(s)$$
$$\text{Pt}(s) + \text{N}_2(g) + 3\ \text{H}_2(g) + \text{I}_2(s) \rightleftharpoons \textit{trans}\text{-Pt}(\text{NH}_3)_2\text{I}_2(s)$$

Use the $\Delta G°$ and $\Delta H°$ at 298.15 K to compute the ΔS°_{298}'s of these two reactions.

$$\textit{cis}:\quad \Delta S^{\circ}_{298} = \frac{\Delta H^{\circ}_{298} - \Delta G^{\circ}_{298}}{T} = \frac{(-286.56\ \text{kJ}) - (-130.25\ \text{kJ})}{298.15\ \text{K}} = -0.52427\ \text{kJ K}^{-1}$$
$$\textit{trans}:\quad \Delta S^{\circ}_{298} = \frac{\Delta H^{\circ}_{298} - \Delta G^{\circ}_{298}}{T} = \frac{(-316.94\ \text{kJ}) - (-161.50\ \text{kJ})}{298.15\ \text{K}} = -0.52135\ \text{kJ K}^{-1}$$

These standard entropies of reaction equal the standard entropies of the products less the entropies of the reactants

$$-524.27\ \text{J K}^{-1} = 1(S^{\circ}_{298},\ \textit{cis}) - 1(41.63) - 1(191.50) - 3(130.57) - 1(116.14)$$
$$-521.35\ \text{J K}^{-1} = 1(S^{\circ}_{298},\ \textit{trans}) - 1(41.63) - 1(191.50) - 3(130.57) - 1(116.14)$$

where the numbers in parentheses are molar $S°$ values (Appendix D) for Pt(*s*), $N_2(g)$, $H_2(g)$, and $I_2(s)$ respectively, and the other numbers are the appropriate numbers of moles. Solving gives S°_{298} (*cis*) as 216.71 J K^{-1}mol^{-1} and S°_{298} (*trans*) as 219.63 J K^{-1}mol^{-1}.

13.62 **a)** The value for $\Delta H°$ computed by the student is for a process at 25°C. The value in the table is for the same change, but at a different temperature, the boiling point of the carbon tetrachloride. Interestingly, the $\Delta H°$ of vaporization of a liquid substance decreases with increasing T and becomes zero at T_c, the critical temperature.
b) At the boiling point of the CCl_4

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{30.0\ \text{kJ mol}^{-1}}{349.65\ \text{K}} = 0.0858\ \text{kJ K}^{-1}\text{mol}^{-1} = 85.8\ \text{J K}^{-1}\text{mol}^{-1}$$

Note that the answer approximates 88 J K^{-1}mol^{-1}, the prediction of Trouton's rule.

13.64 In a reversible adiabatic expansion of a gas, the temperature decreases, so the molecules move more slowly on average. Although molecules have more positions available to them (because the volume has increased), they have fewer velocities. These effects cancel each other out, causing the number of microstates (and thus the entropy) to remain constant.

Chapter 14

Chemical Equilibrium

14.2 **a)** $\frac{(P_{Cl_2O})^2}{(P_{Cl_2})^2 P_{O_2}} = K$ **b)** $\frac{(P_{NOBr})^2}{P_{N_2} P_{O_2} P_{Br_2}} = K$ **c)** $\frac{(P_{H_2O})^4 (P_{CO_2})^3}{P_{C_3H_8} (P_{O_2})^5} = K$

14.4 The equation is $4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 6\ H_2O(g) + 4\ NO(g)$; the corresponding equilibrium expression is

$$\frac{(P_{NO})^4 (P_{H_2O})^6}{(P_{NH_3})^4 (P_{O_2})^5} = K$$

14.6 **a)** The equilibrium expression that goes with the given equation is

$$\frac{P_{COCl_2}}{P_{CO} P_{Cl_2}} = K$$

b) $P_{COCl_2} = K\, P_{CO}\, P_{Cl_2} = (0.20)(0.0020)(0.00030) = 1.2 \times 10^{-7}$ atm

14.8 **a)** When $P_{N_2O_4}$ is graphed against $(P_{NO_2})^2$, the points define a nearly straight line. The slope of this line is the numerical value of K for the reaction $2\ NO_2 \rightleftharpoons N_2O_4$

b) The seven pairs of equilibrium concentrations give seven different values of K. Their mean is 28.4. The graph can also be fitted by linear least-squares.

14.10 **a)** $\frac{1}{(P_{C_2H_2})^3 (P_{H_2})^3} = K$ **b)** $\frac{(P_{CO})^2}{P_{CO_2}} = K$ **c)** $\frac{(P_{HF})^4 P_{CO_2}}{P_{CF_4}} = K$ **d)** $P_{F_2} = K$

14.12 **a)** $\frac{[OH^-]^8 [I_2]^3}{[I^-]^6 [MnO_4^-]^2} = K$ **b)** $\frac{[I_2]}{[Cu^{2+}]^2 [I^-]^4} = K$ **c)** $\frac{[H_3O^+]^2}{P_{O_2}^{1/2} [Sn^{2+}]} = K$

14.14 An acceptable equation is $C_2H_6(g) \rightleftharpoons C_2H_2(g) + 2\ H_2(g)$. The ΔG°_{298} for this reaction is

$$\Delta G^\circ_{298} = 2\underbrace{(0)}_{H_2(g)} + 1\underbrace{(209.20)}_{C_2H_2(g)} - 1\underbrace{(-32.89)}_{C_2H_6(g)} = 242.09 \text{ kJ}$$

The ΔG^0_{298} is related to the equilibrium constant of the reaction at 298 K by $\Delta G^\circ_{298} = -RT \text{ In } K_{298}$. Hence:

$$242.09\times10^3 \text{ J mol}^{-1} = -RT \text{ In } K_{298} = -(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(298.15 \text{ K}) \text{ In } K_{298}$$

$$\text{In } K_{298} = -97.658 \quad \text{and} \quad K_{298} = 3.87\times10^{-43}$$

If the dehydrogenation reaction is represented with a doubled equation (coefficients 2, 2, and 4), then ΔG° comes out twice as big (because the equation has doubled coefficients) and K is squared.

14.16 Compute the ΔG°_{298} of each reaction and then use the relationship $\Delta G^\circ = -RT \text{ In } K$ with T equal to 298.15 K.

a) $\Delta G^\circ_{298} = 2(-46.0) - 2(0) - 1(0) - 1(0) = -92.0$ kJ, so

$$K_{298} = 1.3\times10^{16} = \frac{(P_{HNO_2})^2}{P_{H_2}P_{N_2}P_{O_2}}$$

b) $\Delta G^\circ_{298} = 1(-604.05) + (-228.59) - 1(-898.56) = 65.92$ kJ, so $K_{298} = 2.8\times10^{-12} = P_{H_2O}$.

c) $\Delta G^\circ_{298} = 1(-301.9) - 1(-147.06) - 4(-26.50) = -48.8$ kJ, so

$$K_{298} = 3.6\times10^8 = \frac{[Zn(NH_3)_4^{2+}]}{[Zn^{2+}][NH_3]^4}$$

14.18 The second equation is the first equation reversed with every coefficient divided by 6. The K for the second equation is accordingly the reciprocal of the K of the first raised to the 1/6 power:

$$K_2 = \left(\frac{1}{32.6}\right)^{\frac{1}{6}} = 0.559$$

14.20 The equation of interest, the third equation written in the problem, is equal to the first added to the reverse of the second. Accordingly, the equilibrium constant for the third reaction equals the equilibrium constant of the first multiplied by the reciprocal of the equilibrium constant of the second:

$$K_3 = K_1(K_2)^{-1} = \frac{K_1}{K_2} = \frac{7.0\times10^3}{38\times10^3} = 0.18$$

14.22 **a)** The equation is $F_3SSF(g) \rightleftharpoons 2SF_2(g)$.

b)

$$\frac{P^2_{SF_2}}{P_{F_3SSF}} = \frac{(1.1\times10^{-4})^2}{(0.0484)} = 2.5\times10^{-7} = K$$

14.24 To calculate the equilibrium constant requires the partial pressures of all three gases at equilibrium. Set up a three-line table:

	$SbCl_5(g) \rightleftharpoons$	$SbCl_3(g) +$	$Cl_2(g)$
Initial partial pressure (atm)	x	0.0	0.0
Change in partial pressure (atm)	$-0.718x$	$+0.718x$	$+0.718x$
Equilibrium partial pressure (atm)	$0.282x$	$0.718x$	$0.718x$

What is different here is that the original partial pressure of $SbCl_5$ is not known and is represented by an x. The total pressure at equilibrium is the sum of the partial pressures of the three gases and equals 1.000 atm:

$$1.000\text{ atm} = P_{SbCl_5} + P_{SbCl_3} + P_{Cl_2} = 0.282x + 0.718x + 0.718x$$

Solving gives $x = 0.582$ atm. The equilibrium partial pressures of the three gases are now readily computed:

$$P_{SbCl_5} = 0.164\text{ atm}; \quad P_{SbCl_3} = P_{Cl_2} = 0.418\text{ atm}$$

Substitution in the equilibrium expression gives

$$\frac{P_{SbCl_3}P_{Cl_2}}{P_{SbCl_5}} = \frac{(0.418)(0.418)}{(0.164)} = 1.07 = K$$

14.26 **a)** The vapor density of the contents of the flask cannot change in this gas-phase reaction. Before any of the NOBr(*g*) has a chance to react

$$P_{NOBr} = \left(\frac{n}{V}\right)RT$$
$$= \left(2.219\text{ g L}^{-1} \times \frac{1\text{ mol}}{109.91\text{ g}}\right)(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})(350\text{ K}) = 0.5798\text{ atm}$$

Setting up a three-line table:

	$NOBr(g) \rightleftharpoons$	$NO(g) +$	$1/2\,Br_2(g)$
Initial partial pressure (atm)	0.5798	0.0	0.0
Change in partial pressure (atm)	$-x$	$+x$	$+1/2x$
Equilibrium partial pressure (atm)	$0.5798 - x$	x	$1/2x$

The final pressure in the flask, the sum of the three partial pressures, is 0.675 atm. It follows that

$$P_{NOBr} + P_{NO} + P_{Br_2} = (0.5798 - x) + x + 1/2x = 0.675$$

The value of x is 0.1904 atm, so the three partial pressures are 0.389 atm, 0.190 atm, and 0.0952 atm at equilibrium.

b) Substituting the equilibrium partial pressures into the proper expression gives the numerical equilibrium constant

$$\frac{P_{Br_2}^{\frac{1}{2}} P_{NO}}{P_{NOBr}} = \frac{(0.0952)^{\frac{1}{2}}(0.190)}{0.390} = 0.15 = K_{350}$$

14.28 **a)** A 10.00 g sample of the isopropyl alcohol (molar mass 60.096 g mol^{-1}) amounts to 0.1664 mol. It exerts a pressure of 0.6174 atm in the 10.00 L container at 452.15 K (179°C), assuming that it behaves ideally. This is *before* the reaction has a chance to occur. The reaction generates acetone and hydrogen at the expense of isopropyl alcohol. Let x represent the decrease in the partial pressure of the isopropyl alcohol as the reaction comes to equilibrium. Then:

	$(CH_3)_2CHOH(g) \rightleftharpoons$	$(CH_3)_2CO(g) +$	$H_2(g)$
Init. pressure (atm)	0.6174	0	0
Change in pressure (atm)	$-x$	$+x$	$+x$
Equil. pressure (atm)	$0.6174 - x$	x	x

Substitution of the equilibrium pressures into the equilibrium constant expression gives

$$\frac{x^2}{(0.6174 - x)} = K = 0.444$$

The applicable root of this equation is $x = 0.3467$, so $P_{acetone} = 0.347$ atm at equilibrium.

b) If there were no reaction the partial pressure of isopropyl alcohol would be 0.6174 atm; the actual partial pressure at equilibrium is 0.6174 – 0.3467 = 0.2707 atm. This means that 0.562 of the isopropyl alcohol has dissociated.

14.30 The partial pressure of the hydrogen iodide is unknown at the moment that the glass vessel is filled. Let it be y. The partial pressures of the two products are both zero at the moment of filling. Attainment of equilibrium reduces the partial pressure of HI, the reactant, by some amount, say, $2x$, and increases the partial pressures of each product by x. This is summarized in the table:

	$2HI(g) \rightleftharpoons$	$H_2(g) +$	$I_2(g)$
Init. pressure (atm)	y	0	0
Change in pressure (atm)	$-2x$	$+x$	$+x$
Equil. pressure (atm)	$y - 2x$	x	x

The total pressure at equilibrium, which is given in the problem, is the sum of the equilibrium partial pressures of the three components of the mixture: $(y-2x) + x + x = 6.45$ atm. Clearly, $y = 6.45$ atm. Substitute the equilibrium partial pressures into the expression for K

$$\frac{x^2}{(6.45 - 2x)^2} = K = 0.0259 \quad \text{so that} \quad \frac{x}{(6.45 - 2x)} = \sqrt{0.0259} = 0.1609$$

Solving this equation gives $x = 0.785$. Hence, $P_{H_2} = P_{I_2} = 0.785$ atm, and $P_{HI} = 4.88$ atm.

14.32 Consider the *reverse* of the reaction given in the problem and write the initial pressures, changes and final partial pressures in the usual way:

	$OF_2(g) \rightleftharpoons$	$F_2(g)+$	$\frac{1}{2}O_2(g)$
Init. pressure (atm)	y	0	0
Change in pressure (atm)	$-x$	$+x$	$+\frac{1}{2}x$
Equil. pressure (atm)	1.00	x	$+\frac{1}{2}x$

In this table, y appears as the unknown initial pressure of the $OF_2(g)$, but is not really needed because, from the equilibrium law:

$$\frac{\left(\frac{1}{2}x\right)^{1/2}x}{1.00} = K = \frac{1}{40.1}$$

Square both sides

$$\left(\frac{1}{2}x\right)x^2 = \left(\frac{1}{40.1}\right)^2$$

from which $x = 0.1075$. The partial pressure of the $F_2(g)$ is 0.107 atm, and the partial pressure of the $O_2(g)$ is half this, 0.0538 atm.

14.34

$$\begin{array}{ccc} 2\ NO_2(g) & \rightleftharpoons\ 2\ NO(g) & +\ O_2 \\ 0.89-2x & 2x & x \end{array}$$

$$\frac{x(2x)^2}{(0.89-2x)^2} = 5.9\times10^{-13}$$

Assume that $2x$ is small compared to 0.89. Then

$$4x^3 \approx 5.9\times10^{-13}(0.89)^2 = 4.67\times10^{-13}$$
$$x \approx 4.9\times10^{-5}$$

It is clear that $2x << 0.89$. Thus at equilibrium

$$P_{NO_2} = 0.89\text{ atm} \qquad P_{NO} = 2x = 9.8\times10^{-5}\text{ atm} \qquad P_{O_2} = x = 4.9\times10^{-5}\text{ atm}$$

14.36 The ratio of the initial pressure of H_2 to N_2 is 3:1 from problem **9.35**.

$$\begin{array}{ccc} N_2(g) & +3\ H_2(g) & \rightleftharpoons 2\ NH_3(g) \\ P_o - x & 3P_o - 3x & 2x \end{array}$$

$$P_{total} = P_o - x + (3P_o - 3x) + 2x = 4P_o - 2x = 1.00$$
$$P_o = 0.25 + 0.50x$$
$$P_{N_2} = P_o - x = 0.25 - 0.50x \qquad P_{H_2} = 3P_o - 3x = 0.75 - 1.50x \qquad P_{NH_3} = 2x$$

Insert these values into the equilibrium expression to obtain

$$\frac{\left(P_{NH_3}\right)^2}{P_{N_2}\left(P_{H_2}\right)^3} = K \quad \text{or} \quad \frac{(2x)^2}{(0.25 - 0.50x)(0.75 - 1.50x)} = 3.19 \times 10^{-4}$$

Ignore the terms in x in the denominator and solve the resulting approximate equation for $x: x \approx 2.9 \times 10^{-3}$ atm. Then, at equilibrium

$$P_{N_2} = 0.25 - 0.50x = 0.25 \text{ atm} \quad P_{H_2} = 0.75 - 1.50x = 0.75 \text{ atm} \quad P_{NH_3} = 2x = 5.8 \times 10^{-3} \text{ atm}$$

14.38 The equilibrium constant for the reaction

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

is 2.40 at 100°C (373.15 K). Data concerning two of the three components of the equilibrium are given in terms of concentrations. Deal with this by noting that the partial pressure of any component in a gaseous mixture is related to its concentration by

$$P_A = \left(\frac{n_A}{V}\right)RT = [A]RT$$

if the mixture obeys Dalton's law and the ideal-gas law. Substitute such concentration terms in the equilibrium expression:

$$K = \frac{P_{Cl_2}P_{SO_2}}{P_{SO_2Cl_2}} = \frac{[Cl_2]RT[SO_2]RT}{[SO_2Cl_2]RT} = \frac{[Cl_2][SO_2]}{[SO_2Cl_2]}RT$$

The partial pressures used in equilibrium expressions in the text always refer to a standard state of 1 atm. Therefore, using R in units of L atm mol^{-1}K^{-1} gives all concentrations in mol L^{-1}. The computation is

$$2.40 = \frac{[6.9 \times 10^{-3}][SO_2]}{[3.6 \times 10^{-4}]}(0.08206)(373.15)$$

Solving gives $[SO_2] = 401 \times 10^{-3}$ mol L^{-1}.

14.40 **a)** Both gases come only from the volatilization of the ammonium carbamate; hence their partial pressures are related: $P_{NH_3} = 2P_{CO_2}$. Also, the sum of the two partial pressures is known: $P_{NH_3} + P_{CO_2} = 0.115$ atm. These two equations in two unknowns are easily solved to

$$P_{NH_3} = 0.0767 \text{ atm and } P_{CO_2} = 0.0383 \text{ atm}$$

b) Insert the two partial pressures in the equilibrium expression to obtain the value of the equilibrium constant

$$\left(P_{NH_3}\right)^2 P_{CO_2} = (0.0767)^2(0.0383) = 2.25 \times 10^{-4} = K$$

14.42 **a)** Set up the equilibrium constant expression, substitute in it, and solve

$$\frac{\left(P_{HI}\right)^2}{P_{H_2}} = 0.345$$

$$\left(P_{HI}\right)^2 = 0.345, P_{H_2} = 0.345\left(1.00\right) = 0.345 \text{ from which } P_{HI} = 0.587 \text{ atm}$$

b) The amount of $I_2(s)$ is unimportant as long as it is in excess

$$\begin{array}{lcl} H_2(g) & + I_2(s) \rightleftharpoons & 2\,HI(g) \\ 4.00 - x & & 2x \end{array}$$

$$\frac{\left(2x\right)^2}{4.00 - x} = K = 0.345 \text{ from which } 4x^2 + 0.345x - 1.38 = 0$$

$$x = \frac{-0.345 \pm \sqrt{\left(0.345\right)^2 + 4\left(4\right)\left(1.38\right)}}{8} = 0.546$$

$$P_{H_2} = 4.00 - x = 3.45 \text{ atm} \quad \text{and} \quad P_{HI} = 2x = 1.09 \text{ atm}$$

14.44 **a)** The equilibrium partial pressures of the two product gases (H_2O and CO_2) must equal each other and add up to 1.648 atm; they both equal 0.824 atm. Insert these two partial pressures in the equilibrium expression to get K

$$K = P_{H_2O}P_{CO_2} = \left(0.824\right)\left(0.824\right) = 0.679$$

b) $P_{H_2O} = K/P_{CO_2} = 0.697/0.800 = 0.849$ atm

14.46 **a)** Although the reaction quotient Q has the form of the equilibrium expression, it equals K numerically only if true equilibrium partial pressures are inserted in it. In the situation described, the system is not at equilibrium because Q differs from K:

$$\frac{\left(P_{SF_2}\right)^2}{P_{F_3SSF}} = Q = \frac{\left(2.3\times10^{-4}\right)^2}{0.0484} = 1.1\times10^{-6}$$

The argon takes no part in the reaction and is immaterial to this computation.

b) The value of Q exceeds K, which from problem **14.22** equals 2.5×10^{-7}. The reaction tends to proceed to the left, generating F_3SSF and consuming SF_2, until Q becomes equal to K.

14.48 Substitute the four partial pressures into the reaction quotient expression. At the moment of mixing

$$Q = \frac{P_{NO}P_{CO_2}}{P_{NO_2}P_{CO}} = \frac{\left(1.4\right)\left(1.4\right)}{\left(3.4\right)\left(3.4\right)} = 0.17$$

The K for this reaction must exceed 0.17 because brown NO_2 is consumed as Q tends to become equal to K. This change increases the numerator and decreases the denominator in the equilibrium expression.

14.50 The reaction quotient has the form

$$Q = \frac{\left(P_{HI}\right)^2}{P_{H_2S}P_{I_2}}$$

a) Putting the values given in the problem into the expression gives $Q = 0$; only reactants are present. Some solid sulfur must be produced to reach equilibrium.

b) For this set of initial conditions $Q = 3.5 \times 10^3$, which exceeds K. Solid sulfur is consumed by the reaction coming to equilibrium.

14.52 **a)** The reaction proceeds to the right to reach equilibrium because initially

$$Q = \frac{P_{SO_2} P_{Cl_2}}{P_{SO_2Cl_2}} = \frac{0}{1.20} = 0$$

b)

$$\begin{array}{ccccc} SO_2Cl_2(g) & \rightleftharpoons & SO_2(g) & + & Cl_2(g) \\ 1.20-x & & x & & x \end{array}$$

$$\frac{x^2}{1.20 - x} = 2.4 \quad \text{from which} \quad x^2 + 2.4x - 2.88 = 0$$

$$x = \frac{-2.4 \pm \sqrt{(2.4)^2 + 4(2.88)}}{2} = 0.88$$

$$P_{SO_2} = P_{Cl_2} = 0.88 \text{ atm} \quad P_{SO_2Cl_2} = 1.20 - 0.88 = 0.32 \text{ atm}$$

c) Reduction of the system volume causes net formation of SO_2Cl_2.

14.54 **a)** If $O_2(g)$ is added to the equilibrium $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ at constant V and T, the equilibrium shifts to the left.

b) If the mixture is compressed at constant T, the equilibrium shifts to the left.

c) The equilibrium shifts to the left.

d) Pumping a non-reactive gas into the equilibrium mixture at constant T and P must expand the container. Increasing the volume favors the products.

e) When an inert gas is pumped in at constant V, the total pressure rises, but the partial pressures of the reactants and products are unchanged; the position of the equilibrium is unaffected.

14.56 **a)** The reaction is endothermic because K increases with increasing T.
b) The equilibrium shifts to the left (favoring the reactants) when the non-reactive gas neon is added in such a way that the volume increases. This means that the reactants take up more volume and must have more moles of gas than the product side. There is a net decrease in the number of gas molecules in the reaction.

14.58 Because the reaction is exothermic (giving off heat) a high yield of product is favored by using a low temperature. In addition, the chemical amount of gas decreases in the course of the reaction, so high total pressure favors production of methanol.

14.60 The computation of ΔH^0_{298} and ΔS^0_{298} the formation of dimethyl ether from methanol follows the usual pattern:

$$\Delta H^0_{298} = 1(-241.82) + 1(-184.05) - 2(-200.66) = -24.55 \text{ kJ}$$
$$\Delta S^0_{298} = 1(188.72) + 1(266.27) - 2(239.70) = -24.41 \text{ J K}^{-1}$$

The equilibrium production of dimethyl ether by this means is favored by low temperatures. Pressure has little effect on K.

14.62 Use the van't Hoff equation. Doing so makes the assumption that ΔH^0 and ΔS^0 stay nearly constant between 28 and 48° C. The subscripts giving T are accordingly omitted

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{40}{2900}\right) = \frac{-\Delta H^0}{8.3145 \text{ J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{(273.15+48)\text{K}} - \frac{1}{(273.15+28)\text{K}}\right)$$

Solving gives $\Delta H^0 = -1.7 \times 10^5 \text{ J mol}^{-1}$. Eliminate ΔG^0 between $-RT \ln K = \Delta G^0$ and $\Delta G^0 = \Delta H^0 - T\Delta S^0$ and solve for ΔS^0. Then substitute ΔH^0 and either one of the two K's along with its corresponding T

$$\begin{aligned}\Delta S^0 &= R \ln K + \frac{\Delta H^0}{T} \\ &= \left(8.3145 \text{ J K}^{-1}\text{mol}^{-1}\right)\ln 2900 + \frac{-172\ 288 \text{ J mol}^{-1}}{301.15 \text{ K}} \\ &= \left(66.287 - 571.90\right) \text{ J K}^{-1} \text{ mol}^{-1} = -5.1\times 10^2 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

The "per mole" in the answers refers to moles of the reaction as it is written.

14.64 The reaction is exothermic because K goes down with higher T. Substitute the two temperatures (on the Kelvin scale) and the two K's into the van't Hoff equation

$$\ln\left(\frac{93.1}{2780}\right) = \frac{-\Delta H^0}{R}\left(\frac{1}{(42+273.15)\text{K}} - \frac{1}{(22+273.15)\text{K}}\right)$$

Solving gives $\Delta H^0 = -1.313 \times 10^5 \text{J mol}^{-1}$ or -130 kJ mol^{-1}. To estimate ΔS^0, proceed as in problem **14.62**. Write

$$\Delta S^0 = R \ln K + \frac{\Delta H^0}{T}$$

and substitute using the just obtained ΔH^0 and either of the two K,T pairs. A common error is to use kilojoules in ΔH^0 but joules in R. The answer is $\Delta S^0 = -380 \text{ J K}^{-1} \text{ mol}^{-1}$. As in the previous problem, the "per mole" refers to moles of the reaction as it is written.

14.66 Apply Hess's law to the ΔH_f^0 data from Appendix D and calculate that $\Delta H^0 = -98.89$ kJ for the reaction given. That is, $\Delta H^0 = -98.89$ kJ mol^{-1}. Then use the van't Hoff equation, taking T_2 to be 823 K (550°C),

$$\ln\left(\frac{K_{823}}{K_{298}}\right) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{823\text{ K}} - \frac{1}{298\text{ K}}\right)$$
$$= \left(\frac{-\left(-98890\text{ J mol}^{-1}\right)}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\right)\left(\frac{1}{823\text{ K}} - \frac{1}{298\text{ K}}\right) = -25.46$$
$$\frac{K_{823}}{K_{298}} = e^{-25.46} = 8.75\times 10^{-12}$$
$$K_{823} = \left(9\times 10^{-12}\right)\times\left(2.6\times 10^{12}\right) = 2\times 10^{1}$$

This result differs somewhat from the experimental K_{823} because the temperature dependence of ΔH^0 and ΔS^0 was neglected over quite a large range of temperature. Because the reaction is exothermic, an increase in temperature reduces the equilibrium constant.

14.68 **a)** Substitute in the following special-case version of the van't Hoff equation

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\ln\left(\frac{0.5263\text{ atm}}{0.1316\text{ atm}}\right) = \frac{-\Delta H_{\text{vap}}}{8.3145\text{ J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{373.95\text{ K}} - \frac{1}{343.25\text{ K}}\right)$$
$$\Delta H_{\text{vap}} = 48.2\text{ KJ mol}^{-1}$$

Enthalpies of vaporization are always positive.

b) Set P_2 equal to exactly 1 atm (which is the pressure for normal boiling points) and T_2 equal to T_b

$$\ln\left(\frac{1.000}{0.1316}\right) = \frac{-48.19\times 10^{3}\text{ kJ mol}^{-1}}{8.3145\text{ J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{T_b} - \frac{1}{343.25\text{ K}}\right)$$

Solving for T_b gives $T_b = 390$ K, which is equivalent to 117°C. Substitution of the other P, T pair (0.5263 atm and 373.95 K) for P_2 and T_2 in the equation gives the same answer.

14.70 **a)** In the van't Hoff equation

$$\ln\frac{K_2}{K_1} = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

the two K's are $K_1 = 4.5\times 10^{-19}$ and $K_2 = 6.2\times 10^{-12}$ and $T_1 = 1000$ K and $T_2 = 1200$ K. Substitution and solution gives ΔH° equal to 8.2×10^{5} J mol^{-1}. The "per mole" in the answer refers to per mole of the reaction as written.

b) Another substitution of K's and T's in the van't Hoff equation gives a ΔH° equal to 1.6×10^{6} J mol^{-1}. The ΔH^0 of the reaction written with doubled coefficients is twice as large, as thermodynamics requires.

14.72 The equilibrium concentration of iodine in the aqueous layer is given as 4.169×10^{-5} M; the volume of this layer is not given. Suppose that it is V L. Then the chemical amount of I_2 in the aqueous layer at equilibrium is $(4.16\times10^{-5}\,V)$ mol. Before equilibrium (before the mixture was shaken), the amount of I_2 in the aqueous layer was much larger. It was $(2.50\times10^{-2}\,V)$ mol. The amount of I_2 transferred to the CS_2 layer in attaining the partition equilibrium was

$$\left((2.50\times10^{-2})-(4.16\times10^{-5})\right)\text{ mol L}^{-1}\times\ V\text{ L}\ \approx\ (2.50\times10^{-2})V\text{ mol}$$

The concentration of the iodine in the CS_2 layer is this chemical amount divided by the volume of the CS_2, which equals V L. It is therefore 2.50×10^{-2} mol L^{-1}. The partition equilibrium constant is

$$\frac{[I_2]_{(CS_2)}}{[I_2]_{(aq)}}=\frac{2.50\times10^{-2}}{4.16\times10^{-5}}=600=K$$

14.74 **a)** The equilibrium constant for the dissolution of the citric acid according to the equation given in the problem is, in simple theory, just the concentration of the dissolved citric acid. For citric acid $\mathcal{M}$ is 192.1 g mol^{-1}, so the saturated aqueous solution contains 6.77 mol L^{-1} and $K=6.8$. This assumes that there is no ionization of the citric acid in water and also that this concentrated solution behaves ideally. Neither assumption is very defensible. The K for the dissolution in ether is, by similar reasoning, 0.11.

b) The transfer of citric acid from water into ether equals the reverse of the dissolution of citric acid in water added to the dissolution of citric acid in ether. The partition coefficient K is therefore $0.11/6.8=0.017$.

14.76 The synthetic reaction is

$$CO(g)+2\ H_2(g)\rightleftharpoons CH_3OH(g)\ \text{with}\ \frac{P_{CH_3OH}}{P_{CO}\left(P_{H_2}\right)^2}=6.08\times10^{-3}\ \text{at }225°C$$

Let the equilibrium partial pressure of the H_2 be $2x$; then $P_{co}=x$. Meanwhile, the partial pressure of the methanol equals 0.500 atm. Substitution gives:

$$\frac{0.500}{x(2x)^2}=6.08\times10^{-3}$$

Solving for x gives 2.74. The equilibrium partial pressure of the CO is 2.74 atm; the equilibrium partial pressure of the H_2 is 5.48 atm.

14.78 **a)** To calculate the degree of conversion of the *t*-butanol requires knowledge of its partial pressure at equilibrium. Set up a three-line table:

	$(CH_3)_3COH(g)\rightleftharpoons$	$(CH_3)_2CCH_2(g)+$	$H_2O(g)$
Init. Preasure (atm)	0.100	0.0	0.0
Change in preasure (atm)	$-x$	$+x$	$+x$
Equil. Pressure (atm)	$0.100-x$	x	x

Putting the equilibrium values into the equilibrium law gives

$$\frac{x^2}{(0.100 - x)} = K = 2.42$$

from which x is 0.0962 atm. The fraction of *t*-butanol that is converted at equilibrium is 0.0962 atm/0.100 atm = 0.962.

b) Replacing the initial pressure 0.100 atm with 5.00 atm and carrying out a similar calculation gives $x = 2.473$, so the fraction converted is 2.473 atm/5.00 atm = 0.495.

14.80 **a)** Let y stand for the equilibrium partial pressure of the acetic acid dimer and x stand for the equilibrium partial pressure of the monomer. According to the problem, the sum of these two partial pressures is 0.725 atm, that is, $x + y = 0.725$. Also, the two partial pressures are related by the equilibrium law

$$\frac{P_{\text{dimer}}}{(P_{\text{monomer}})^2} = \frac{y}{x^2} = 3.72$$

Eliminate x between the two equations and solve (by means of the quadratic formula) to obtain y = 0.398 atm. This is the equilibrium partial pressure of the dimer.

b) Solving for x in the previous part gives the equilibrium partial pressure of the monomeric acetic acid as 0.327 atm. If none of the acetic acid were dimerized, the partial pressure of the monomer would be $0.327 + (2 \times 0.398) = 1.123$ atm. The pressure of monomer that is actually present is 0.327 atm. This is 29.1% of 1.123 atm; it follows that 70.9% of the acetic acid is present as the dimer.

14.82 Compute the initial amount of SO_3 in the system

$$\frac{0.800\,g}{80.063\,g \text{ mol}^{-1}} = 9.99 \times 10^{-3} \text{ mol } SO_3$$

Its initial partial pressure is

$$P = \frac{nRT}{V} = \frac{(9.99 \times 10^{-3} \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(900 \text{ K})}{0.1000 \text{ L}} = 7.38 \text{ atm}$$

$$\underset{\frac{1}{2}x}{\tfrac{1}{2}O_2(g)} + \underset{x}{SO_2(g)} \rightleftharpoons \underset{7.38-x}{SO_3(g)} \qquad \frac{P_{SO_3}}{P_{SO_2}\sqrt{P_{O_2}}} = K$$

Substitute the equilibrium partial pressures into the equilibrium constant expression

$$\frac{7.38 - x}{x\sqrt{x/2}} = K = 0.587$$

This can be rearranged to $x^3 - 5.8081x^2 + 85.7275x - 316.335 = 0$. Solve this cubic equation with a hand-held calculator. It has a single real root: $x = 4.03$. Therefore $P_{O_2} = x/2 = 2.01$ atm. This root can also be quickly discovered by systematically trying out values for x between 0 and 7.38 in the original equation.

14.84 The second equation is the first reversed and multiplied through by 2. Hence, $K_2 = 1/K_1^2$. The subscripts refer to the equations in the order given in the problem.

14.86 Write the equilibrium law for the reaction of KOH(*s*) with $CO_2(g)$ to give $KHCO_3(s)$. Two of the three compounds in the equilibrium are solids and do not appear in the expression, which is consequently quite simple:

$$\frac{1}{P_{CO_2}} = K$$

The K is given as 6×10^{15}. Consequently, at equilibrium $P_{CO_2} = 2 \times 10^{-16}$ atm. The amounts of the two solids are immaterial as long as some of each is present at equilibrium.

14.88 **a)** According to the balanced equation, one mole of fructose forms for every one mole of glucose that reacts. At equilibrium in the first experiment, [fructose] = 0.1175 M and [glucose] = 0.2564 − 0.1175 = 0.1389 M. The equilibrium constant is the ratio of these two numbers, which is 0.8459. In the second experiment, equilibrium is approached from the other direction. At equilibrium [fructose] = 0.2666 − 0.1415 = 0.1251 M and [glucose] = 0.1415 M. The K is 0.8841, which is within 5% of the other result. (These are published experimental data.) The average K is 0.865.
b) Use the average equilibrium constant from part **a)**. If x is the fraction of glucose converted, then at equilibrium [fructose] = $x\ c_0$ where c_0 is the initial concentration. Then [glucose] = $(1 - x)\ c_0$ and $x/(1 - x)$. Solving for x gives 0.464, so 46.4% of the glucose is converted.

14.90 A process can be quite exothermic, but still non-spontaneous. At constant T and P the condition for spontaneity is the sign of ΔG. Under these conditions, spontaneity is a compromise between two terms, an enthalpy term ΔH and an entropy term $-T\Delta S$. If ΔS is negative, then $-T\Delta S$ is positive. A large enough T forces ΔG to become positive. The more negative the ΔS, then the lower is the required temperature. The fact that helium is only slightly soluble in $H_2O(l)$ means that $-T\Delta S$ for $He(g) \rightarrow He(aq)$ overmatches the negative ΔH. That is possible only if ΔS is negative.

14.92 Decomposition of peroxydisulfuryl difluoride (the dimer) creates 2 mol of gas from every 1 mol of gas that reacts. If the dimer decomposed significantly during the temperature change from 100° to 110°C, then the pressure of the sample would increase more than 2.7%, which is the increase based just on the ideal-gas law

$$\frac{P_2}{P_1} \propto \frac{T_2}{T_1} = \frac{(273.15 + 110)\ \text{K}}{(273.15 + 110)\ \text{K}} = 1.027$$

The only conclusion is that the proportion of FO_2SO (the monomer) in the sample was small after the temperature increase, and even smaller before the temperature increase (higher temperature favors the dark-colored monomer). Although the proportion of the monomer remains small throughout the experiment, it nevertheless doubles between 100° and 110° according to the change in the intensity of the brown color. With these points in mind, write the equilibrium law for the reaction dimer $\rightleftharpoons$ 2 monomer. The form of the law is the same at the two temperatures. At 100°C it is

$$K_{373} = \frac{(P_{\text{monomer}})^2}{P_{\text{dimer}}} = \frac{(n/V_{\text{monomer}})^2 (RT)^2}{(n/V_{\text{dimer}})RT} = \frac{[\text{monomer}]^2}{[\text{dimer}]} RT = \frac{[\text{monomer}]^2}{[\text{dimer}]}(373.15)R$$

which uses the fact that $P = (n/V)RT$ for each component. At 110°C it is

$$K_{383} = \frac{P^2_{\text{monomer}}}{P_{\text{dimer}}} = \frac{\left[\text{monomer}\right]^2}{\left[\text{dimer}\right]}\left(383.15\right)R$$

Construct the ratio of these two K's to use in the van't Hoff equation. Dividing the second equation by the first gives

$$\frac{K_{383}}{K_{373}} = \left(\frac{\left[\text{monomer}\right]_{383}}{\left[\text{monomer}\right]_{373}}\right)^2\left(\frac{\left[\text{dimer}\right]_{373}}{\left[\text{dimer}\right]_{383}}\right)\left(\frac{383.15\text{ K}}{373.15\text{ K}}\right)$$

The concentration of monomer doubles with the temperature increase so the first term in parentheses equals 2. The second term essentially equals 1 because the amount of the dimer in the container hardly changes. Thus:

$$\frac{K_{383}}{K_{373}} = \left(2^2\right)\times\left(1\right)\times\left(\frac{383.15}{373.15}\right) = 4.11$$

Substitution in the van't Hoff equation gives

$$\ln\frac{K_{383}}{K_{373}} = \ln 4.11 = \frac{-\Delta H°}{R}\left(\frac{1}{383.15} - \frac{1}{373.15}\right)$$

and the molar $\Delta H°$ of the reaction is easily computed. It is $\Delta H° = 168\text{ kJ mol}^{-1} = 1.7 \times 10^2\text{ J mol}^{-1}$.

14.94

$$K_1 = \frac{\left[\text{benzoic acid}\right]_{(ether)}}{\left[\text{benzoic acid}\right]_{(aq)}} = 330 \quad \text{and} \quad K_2 = \frac{\left[\text{citric acid}\right]_{(ether)}}{\left[\text{citric acid}\right]_{(ag)}} = 1.69\times10^{-2}$$

Ether and water are nearly immiscible; they form layers when mixed. The data mean that when the 50 : 50 mixture of citric acid and benzoic acid is treated with the mixture of ether and water, most of the benzoic acid ends up in the ether, and most of the citric acid ends up in the water.

Let x equal the mass of the benzoic acid present in the water at equilibrium. Then $1.00 - x$ is the mass of benzoic acid present in the ether. Similarly, let y be the mass of the citric acid present in the water at equilibrium. Then $1.00 - y$ is the mass of citric acid in the ether. The equilibrium laws for the partition of the two organic acids involve concentrations, not amounts. In this problem, the volumes of the two solvents are equal, so the amounts of the solutes in the two layers have the same ratios as their concentrations. Then:

$$\frac{1.00 - x}{x} = 330 \quad \text{and} \quad \frac{1.00 - y}{y} = 1.69\times10^{-2}$$

Solving the equation in x shows that there is 3.0×10^{-3} g of benzoic acid in the water at equilibrium and 0.9970 g of benzoic acid in the ether. From the equation in y, there is 0.9834 g of citric acid in the water at equilibrium and 0.0166 g of citric acid in the ether. The total mass of the solids in the ether is 1.0136 g, of which 0.9970 g is benzoic acid. The benzoic acid is therefore 98.4 % of the dissolved solids in the ether. The total mass of the solids in the water is 0.9864 g, of which 0.9834 g is citric acid. The citric acid is 99.7 % of the solid recovered from the water layer.

14.96

$6\,CH_4(g)+$	$\frac{9}{2}O_2(g)\rightarrow$	$C_6H_6(l)+$	$9\,H_2O(l)$	
−74.81	0.00	49.03	−285.83	ΔH_f° (kJ mol^{-1})
−50.75	0.00	124.50	−237.18	ΔG_f° (kJ mol^{-1})

$$\Delta H^\circ = 9(-285.83) + 49.03 - 6(-74.81) = -2074.58 \text{ kJ}$$
$$\Delta G^\circ = 9(-237.18) + 124.50 - 6(-50.75) = -1705.62 \text{ kJ}$$
$$K = \exp(-\Delta G^\circ / RT) = 10^{299}$$

14.98 The initial chemical amount of methanol is 0.1473 mol, so its initial partial pressure, calculated from the ideal-gas law, is 6.324 atm. Suppose this is reduced by x atm at equilibrium, giving an equilibrium partial pressure of $2x$ atm for $H_2(g)$. According to Graham's law of effusion (text Section 9.8), the ratio of effusion rates of two gases from a single container is

$$\frac{\text{rate of effusion of } H_2}{\text{rate of effusion of } CH_3OH} = \frac{N_{H_2}}{N_{CH_3OH}}\sqrt{\frac{\mathcal{M}_{CH_3OH}}{\mathcal{M}_{H_2}}}$$

The problem states that the ratio on the left side of this equation is 33, and the molar masses are easily calculated. The ratio of the number of molecules is equal to the ratio of partial pressures, because volume and temperature are the same. Thus,

$$33 = \frac{2x}{6.324 - x}\sqrt{\frac{32.04}{2.016}}$$

Solving this gives x = 5.093. The equilibrium partial pressures are thus $P_{CO} = x = 5.093$ atm, $P_{H_2} = 2x = 10.19$ atm, and $P_{CH_3OH} = 6.324 - x = 1.231$ atm. Divide each of these partial pressures by 1 atm (the standard-state pressure and substitute into the equilibrium constant expression

$$K = \frac{P_{CO}(P_{H_2})^2}{P_{CH_3OH}} = \frac{5.093(10.19)^2}{1.231} = 4.3 \times 10^2$$

14.100 Compute the equilibrium partial pressure of water vapor above a sample of $CaSO_4 \cdot 2H_2O$ at 25°C

$$\frac{1}{(P_{H_2O})^2} = K_{298} = 1.6 \times 10^3$$
$$P_{H_2O} = 0.025 \text{ atm}$$

From text Table 10.3 (not 10.1) the equilibrium partial pressure of water above a sample of liquid water at 25°C is 0.03126 atm. This partial pressure corresponds to a relative humidity of 100%. The threshold relative humidity for the conversion of $CaSO_4$ to its dihydrate is then $0.025/0.03126 \times 100\% = 80\%$. Above this value $Q < K$ for the hydration reaction.

14.102 a) For the vaporization of 1 mol of liquid benzene to vaporous benzene at 25°C,

$$\Delta H^\circ_{298} = 82.93 - 49.03 = 33.90 \text{ kJ} \quad \text{and} \quad \Delta G^\circ_{298} = 129.66 - 124.50 = 5.16 \text{ kJ}$$

The numerical data come from Appendix D.

b) Let P equal the vapor pressure at 25°C. Then for the vaporization

$$\Delta G_{298} = \Delta G^{\circ}_{298} + RT \ln P$$
$$\text{In } P = \frac{\Delta G_{298}}{RT} - \frac{\Delta G^{\circ}_{298}}{RT}$$

When the liquid reaches equilibrium with its vapor at 25°C, then ΔG_{298} equals zero

$$\text{In } P = 0 - \frac{\Delta G^{\circ}_{298}}{\left(8.3145 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(298.15 \text{ K}\right)}$$
$$= -\frac{5160 \text{ J}}{2479 \text{ J}} = -2.081$$
$$P = 0.125 \text{ atm}$$

c) $\Delta S^{\circ}_{\text{vap}} = \left(\Delta H^{\circ} - \Delta G^{\circ}\right)/T = 96.4 \text{ J K}^{-1}$. The normal boiling point is the temperature at which

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{33.90 \times 10^{3} \text{ J}}{96.4 \text{ J K}^{-1}} = 352 \text{ K}$$

This is 79°C. The actual normal boiling point is 80.1°C.

14.104 a) The sublimation of $NbI_5(s)$ is described by

$$NbI_5(s) \rightleftharpoons NbI_5(g) \quad K = P_{NbI_5}$$

where K depends on the temperature according to the equation:

$$\ln K = -\frac{\Delta H^{\circ}_{\text{subl}}}{RT} + \frac{\Delta S^{\circ}_{\text{subl}}}{R}$$

Substituting the equilibrium expression into this equation gives

$$\ln P_{NbI_5} = -\frac{\Delta H^{\circ}_{\text{subl}}}{RT} + \frac{\Delta S^{\circ}_{\text{subl}}}{R}$$

The natural logarithm of a number is 2.3026 times the common (base 10) logarithm

$$2.3026 \log P_{NbI_5} = -\frac{\Delta H^{\circ}_{\text{subl}}}{RT} + \frac{\Delta S^{\circ}_{\text{subl}}}{R}$$

The problem gives an expression for the dependence of $\log P_{NbI_5}$ on T. Insert it on the left

$$2.3026\left(\frac{-6762}{T} + 8.566\right) = -\frac{\Delta H^{\circ}_{\text{subl}}}{RT} + \frac{\Delta S^{\circ}_{\text{subl}}}{R}$$

From term-by-term comparison of the two sides of this equation

$$\Delta H^{\circ}_{\text{subl}} = 2.3026\left(6762\ R\right) \quad \text{and} \quad \Delta S^{\circ}_{\text{subl}} = 2.3026\left(8.566\ R\right)$$

$$\Delta H^{\circ}_{\text{subl}} = 129.5 \times 10^{3} \text{ J mol}^{-1} \quad \text{and} \quad \Delta S^{\circ}_{\text{subl}} = 164.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note that "-6762" (and "-4653") in the problem actually have units of kelvins. The "8.566" (and "5.43") are dimensionless.

b) A similar analysis for the vaporization of the $NbI_5(l)$ gives

$$\Delta H^\circ_{vap} = 89.08 \times 10^3 \text{ J mol}^{-1} \quad \text{and} \quad \Delta S^\circ_{vap} = 104 \text{ J K}^{-1}\text{mol}^{-1}$$

c) The normal boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid equals 1 atm. Therefore

$$\log 1 = 0 = \frac{-4653}{T_b} + 5.43 \quad \text{from which} \quad \text{T}_b = 857 \text{ K}$$

d) According to the hint, the vapor pressures of the liquid and solid NbI_5 are equal at the triple point. Simply equate the expressions that give the temperature dependence of these quantities and subscript the temperature as the triple point:

$$\frac{-6762}{T_t} + 8.566 = \frac{-4653}{T_t} + 5.43$$

Solving gives the triple point temperature as 673 K. The pressure at this point is found by solving either of starting equations for P. The result is $P_t = 0.0324$ atm.

14.106 The reaction is $\text{allene}(g) \rightarrow \text{propyne}(g)$

$$\Delta H^\circ = 185 - 192 = -7 \text{ kJ}$$
$$\Delta G^\circ = 194 - 202 = -8 \text{ kJ} = -RT \ln K$$
$$\ln K = \frac{8 \times 10^3 \text{ J}}{\left(8.3145 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(298 \text{ K}\right)}$$
$$K = e^{3.23} = 3 \times 10^1$$

14.108 a) The reaction is the isomerization of butane to isobutane: B $\rightarrow$ I.

$$\Delta G^\circ_f = -18.0 - \left(-15.9\right) \text{ kJ} = -2.1 \text{ kJ}$$

The means that isobutane is more stable than butane (at 298 K and 1 atm pressure).

$$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f; \quad \Delta S^\circ_f = \frac{1}{T}\left(\Delta H^\circ_f - \Delta G^\circ_f\right)$$
$$\Delta S^\circ_f\left(\text{B}\right) = \frac{-124.7 - \left(-15.9\right)}{298.15 \text{ K}} \times 10^3 \text{ J mol}^{-1} = -365 \text{ J K}^{-1}\text{mol}^{-1}$$
$$\Delta S^\circ_f\left(\text{I}\right) = \frac{-131.3 - \left(-18.0\right)}{298.15 \text{ K}} \times 10^3 \text{ J mol}^{-1} = -380 \text{ J K}^{-1}\text{mol}^{-1}$$

Butane has a higher (more positive) entropy than isobutane.

b)

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{2.1 \times 10^3 \text{ J mol}^{-1}}{\left(8.31 \text{ J K}^{-1}\text{mol}^{-1}\right)298 \text{ K}} = 0.85 \quad K = 2.3$$

Let X be the fraction of B. Then $(1-X)$ is the fraction of I. Then

$$K = \frac{1-X}{X} = 2.3 \quad 2.3X = 1-X \quad X = \frac{1}{3.3} = 0.30$$

The percentage of B in the equilibrium mixture is therefore 30%.

14.110 a) $P_{CO} = 1.00 \text{ atm} \times 0.983 = 0.983$ atm. Similarly, $P_{CO_2} = 0.0169$ atm.

b) $K_{1200} = P^2_{CO} / P_{CO_2} = 57.2$ (last digit is very uncertain)

c) $\Delta G^\circ_{1200} = -RT \ln K = -\left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(1200 \text{ K}\right) \text{ In } 57.2 = -40.4 \text{ kJ} \approx -40 \text{ kJ}$

14.112 The three gases are formed in the molar ratio 2 : 1 : 1; consequently their partial pressures are in the same ratio. The total pressure is 0.400 atm

$$P_{NH_3} = 0.200 \text{ atm} \quad P_{CO_2} = 0.100 \text{ atm} \quad P_{H_2O} = 0.100 \text{ atm}$$
$$K = P^2_{NH_3} P_{CO_2} P_{H_2O} = \left(0.200\right)^2 \left(0.100\right)^2 = 4.00 \times 10^{-4}$$

If P_{H_2O} is adjusted "by external means" to equal 0.200 atm in the presence of solid ammonium carbonate, then the equilibrium adjusts to a new position at which

$$P^2_{NH_3} P_{CO_2} = 4.00 \times 10^{-4} / \left(0.200\right) = 2.00 \times 10^{-3}$$

The partial pressure of ammonia would still be twice the partial pressure of carbon dioxide (because the number of moles of ammonia is twice that of carbon dioxide). Let $P_{CO_2} = x$. Then:

$$\left(2x\right)^2 x = 2.00 \times 10^{-3}$$
$$x^3 = 0.500 \times 10^{-3}$$
$$x = 7.9 \times 10^{-2} \text{ atm}$$

Thus $P_{CO_2} = 0.079$ atm and $P_{NH_3} = 0.159$ atm.

Chapter 15

Acid-Base Equilibria

15.2 All five can act as Brønsted-Lowry bases. Their conjugate acids are HF, HSO_4^-, OH^-, H_2O and H_3O^+.

15.4 $NH_3(aq) + CH_3COOH(aq) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$

15.6 **a)** The slag-forming reaction is $CaO + SiO_2 \rightarrow CaSiO_3$.

b) The CaO is a Lewis base and the SiO_2 is a Lewis acid.

15.8 **a)** This problem follows up the extension of the acid-base concepts suggested by problems **15.6** and **15.7**. In the Brønsted system, the acid is the *donor* of a *positively* charged particle (the hydrogen ion); in this system (called the Lux-Flood acid-base system) the acid is the *acceptor* of a *negatively* charged particle (the oxide ion), and the base is the donor of the oxide ion.

b) In the first reaction CaO donates O^{2-} to SiO_2 so CaO is the base, and SiO_2 is the acid. In the second reaction the SiO_2 again accepts an O^{2-} and is again the acid. It accepts the O^{2-} from Ca_2SiO_4, which is the base. In the third reaction, the CaO donates O^{2-} to Ca_2SiO_4. The latter serves as an acid in this reaction, the opposite of its role in the second reaction.

15.10 **a)** The anhydride is As_2O_5, diarsenic pentaoxide.

b) The anhydride of this compound, which is called molybdic acid, is molybdenum(VI) oxide, MoO_3.

c) The anhydride is Rb_2O, rubidium oxide.

d) The anhydride is SO_2, sulfur dioxide.

15.12

$$ZnO(s) + 2\,HCl(aq) \rightarrow Zn^{2+}(aq) + 2\,Cl^{-1}(aq) + H_2O(l)$$
$$ZnO(s) + 2\,NaOH(aq) + H_2O(l) \rightarrow Zn(OH)_4^{2-}(aq) + 2\,Na^+(aq)$$

15.14

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{3.6\times10^{-2}} \quad pH = -\log[H_3O^+] = 12.56$$

15.16 For H_3O^+ ion, the range is 4.5×10^{-8} M to 3.5×10^{-8}. For OH^- ion the range is 2.2×10^{-7} to 2.8×10^{-7} M.

15.18 Compute the concentration of hydronium ion using the definition of pH

$$\left[H_3O^+\right] = 10^{-7.4} = 4\times10^{-8}\ \text{M}$$

To determine the concentration of OH^- use the equilibrium expression for the autoionization of water

$$\left[OH^-\right] = \frac{K_W}{\left[H_3O^+\right]} = \frac{2.4\times10^{-14}}{4\times10^{-8}} = 6\times10^{17}\ \text{M}$$

15.20 Raising the pH increases the concentration of OH^- ions. This makes the direct substitution reaction much more feasible

$$\left(CH_3\right)_3CCl + OH^- \rightarrow \left(CH_3\right)_3COH + Cl^-$$

15.22 **a)** The ionization of niacin proceeds by the reaction

$$C_5H_4NCOOH(aq) + H_2O(l) \rightleftharpoons C_5H_4NCOO^-(aq) + H_3O^+(aq)$$

b) In aqueous solutions, the product of K_a of an acid and K_b of its conjugate base is K_w. Hence

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.5\times10^{-5}} = 6.7\times10^{-10}\ \text{at } 25°\text{C}$$

c) The K_a for the pyridinium ion appears in text Table 15.2. It is 5.6×10^{-6}, smaller than the K_a of niacin. Niacin is a stronger acid than pyridinium ion, which means that its conjugate base is a weaker base than pyridine.

15.24 The equation given in the problem is the sum of the chemical equation for the third acid ionization reaction of phosphoric acid

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

and the reverse of the equation for the first acid ionization of carbonic acid $\left(H_2CO_3\right)$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

Hence, the desired equilibrium constant is

$$K = \frac{K_{a_3,H_3PO_4}}{K_{a_1,H_2CO_3}} = \frac{2.2\times10^{-13}}{4.3\times10^{-7}} = 5.1\times10^{-7}$$

H_2CO_3 is the stronger acid, and PO_4^{3-} is the stronger base.

15.26 **a)** According to text Figure 15.9, cresol red starts its change from its basic to acidic color at a pH of 8.8, but thymolphthalein starts at the less acidic pH of 10.6. The color changes mark the pH at which the concentrations of the acid forms of the indicators start to become important. The basic form of the thymolphthalein requires a lesser concentration of H_3O^+ to cause it to change to the acid form. It is accordingly a stronger base than the basic form of cresol red.

b) Clearly, $8.8 < \text{pH} < 9.4$. See text Figure 15.9.

15.28 The molar mass of ascorbic acid is 176.126 g mol^{-1}. The concentration of ascorbic acid in the 100 mL of water is its chemical amount, 2.839×10^{-3} mol (computed by dividing 500×10^{-3} g by the molar mass) itself divided by the volume of the solution (0.100 L). It is 0.0284 M. The acid-ionization equilibrium is

$$HC_6H_7O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_7O_6^-(aq)$$

for which the equilibrium expression is

$$\frac{[H_3O^+][C_6H_7O_6^-]}{[HC_6H_7O_6]} = K_a = 8.0\times10^{-5}$$

$$\frac{x^2}{0.0284 - x} = 8.0\times10^{-5}$$

Solving the equation gives $x = 1.47\times10^{-3}$. The pH is $-\log(1.47\times10^{-3}) = 2.83$.

15.30 **a)** The K_a of propionic acid is 1.34×10^{-5} (see text Table 15.2). Following the pattern of text Example 15.3 gives the concentration of H_3O^+ as 2.16×10^{-3} M, for a pH of 2.664.

b) A solution of formic acid of pH 2.664 is to be prepared. The K_a of formic acid is 1.77×10^{-4}. Because formic acid is a stronger acid than propionic acid, less of it than propionic acid is required to lower the pH of a liter of pure water from 7.0 to 2.664, a pH corresponding to $[H_3O^+] = 2.16\times10^{-3}$ M. Let the required concentration of formic acid be *c*. Then, at equilibrium

$$1.77\times10^{-4} = \frac{(2.16\times10^{-3})(2.16\times10^{-3})}{(c - 2.16\times10^{-3})}$$

Solving gives $c = 2.85\times10^{-2}$; the required concentration of formic acid is only 2.85×10^{-2} M.

15.32 If the equilibrium concentration of H_3O^+ is *x*, then

$$[C_6F_5COO^-] = x \quad \text{and} \quad [C_6F_5COOH] = 0.100 - x$$

Substitution into the equilibrium expression gives

$$\frac{[H_3O^+][C_6F_5COO^-]}{[C_6F_5COOH]} = K_a = 0.033 = \frac{x^2}{(0.100 - x)}$$

This equation can be solved by the quadratic formula or by iteration to give $x = 0.0433$. The pH is $-\log_{10}(0.0433) = 1.36$.

15.34 From the given pH of the solution (2.42), $[H_3O^+] = 3.8\times10^{-3}$ M. This is also essentially the concentration of the 2-germaacetate ion at equilibrium; the concentration of the unionized

2-germaacetic acid is then $0.050 - (3.8\times10^{-3}) = 0.046$ M. Substitution of these values into the equilibrium expression gives $K_a = 3.1\times10^{-4}$. This exceeds the K_a of acetic acid by a factor of about 17, indicating that 2-germaacetic acid is stronger than acetic acid.

15.36 Represent methylamine as MA. Its initial concentration is (0.070 mol/0.8000 L) = 0.0875 M. It reacts as a base in water

$$\mathrm{MA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HMA^+}(aq) + \mathrm{OH^-}(aq)$$

If x mol L^{-1} of MA reacts, giving $[HMA^+] = [OH^-] = x$, then at equilibrium

$$\frac{x^2}{0.0875 - x} = K_b = 4.4\times10^{-4} \quad \text{from which} \quad x = [\mathrm{OH^-}] = 6.0\times10^{-3}\ \mathrm{mol\ L^{-1}}$$

Assuming that the temperature is 25°C

$$[\mathrm{H_3O^+}] = \frac{K_w}{[\mathrm{OH^-}]} = \frac{1.0\times10^{-14}}{6.0\times10^{-3}} = 1.7\times10^{-12}\ \mathrm{mol\ L^{-1}} \quad \text{and} \quad \mathrm{pH} = 11.78$$

15.38 Cyanide ion reacts with water as a base: $\mathrm{CN^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HCN}(aq) + \mathrm{OH^-}(aq)$.

$$\frac{[\mathrm{OH^-}][\mathrm{HCN}]}{[\mathrm{CN^-}]} = K_b = \frac{K_w}{6.17\times10^{-10}} = 1.6\times10^{-5} \text{ at } 25°\mathrm{C}$$

$$\mathrm{pOH} = 14.00 - 11.50 = 2.50 \quad [\mathrm{OH^-}] = [\mathrm{HCN}] = 10^{-2.50} = 3.2\times10^{-3}$$

$$[\mathrm{CN^-}] = \frac{[\mathrm{OH^-}][\mathrm{HCN}]}{K_b} = 0.62\ \mathrm{mol\ L^{-1}}$$

15.40 The first solution contains (75.00×0.0460) mmol of a strong acid ($HClO_4$); the second contains (150.00×0.0230) mmol of a strong base (KOH). Upon mixing the solutions, the acid and base react to generate water and K^+ and ClO_4^- ions. Neither the acid nor the base is in excess, so neither OH^- nor H_3O^+ remains in excess after the reaction. Neither of the ions acts detectably as an acid or base in water. The pH of the solution equals 7.0.

15.42 Low pH: HBr < NH_4I < NaCl < KF < LiOH :High pH

15.44 Write the reaction of the weak base "bis" in water and the equilibrium expression

$$\mathrm{bis}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{bisH^+}(aq) + \mathrm{OH^-}(aq) \quad K_b = \frac{[\mathrm{OH^-}][\mathrm{bisH^+}]}{[\mathrm{bis}]} = 10^{-8.8}$$

The concentrations of bis and its conjugate acid are essentially equal under the conditions described in the problem because the amount of the HCl that has been added is just enough to convert half of the bis to $bisH^+$ and leave half unreacted. It is true that both of these species then react with water, but the changes in amount caused by these interactions are negligible. Therefore $K_b = [\mathrm{OH^-}]$ and $\mathrm{p}K_b = \mathrm{pOH}$. The pOH is 8.8, and the pH is $14.0 - 8.8 = 5.2$.

15.46 The acid ionization of sulfanilic acid has the equilibrium law

$$\frac{\left[NH_2C_6H_4SO_3^-\right]\left[H_3O^+\right]}{\left[NH_2C_6H_4SO_3H\right]} = K_a = 5.9\times10^{-4}$$

a) Compute the pH by substituting 0.20 M – x for the concentration of sulfanilic acid and 0.13 M + x for the concentration of sulfanilate ion in the preceding, solving for $x = \left[H_3O^+\right]$, and taking the negative logarithm. The pH is 3.04.

b) Adding 0.040 mol of HCl converts 0.040 mol of sulfanilate ion to its conjugate acid, sulfanilic acid. The concentrations of the two become 0.24 M -x and 0.09 M + x, respectively. Substitute and solve as in the previous part. The pH is 2.8.

15.48 The pK_a for the first acid ionization of carbonic acid is 6.37. The pK_a for the second acid ionization of phosphoric acid is 7.21. From the standpoint of suitability for pH control, the $H_2PO_4^-/HPO_4^{2-}$ system would be better because the applicable pK_a is closer to the desired pH.

15.50 The desired concentration of hydronium ion is $\left[H_3O^+\right] = 10^{-9.60} = 2.5\times10^{-10}$ mol L^{-1}.

$$\frac{\left[H_3O^-\right]\left[CN^-\right]}{\left[HCN\right]} = K_a = 6.17\times10^{-10} \quad \text{from which} \quad \frac{\left[CN^-\right]}{\left[HCN\right]} = \frac{6.17\times10^{-10}}{2.5\times10^{-10}} = 2.46$$

The amount of “cyanide stuff” in the solution is (0.400 L) (0.0800 mol L^{-1}) = 0.0320 mol. It is present as either HCN or CN $^-$.

$$n_{HCN} + n_{CN^-} = 0.0320 \text{ mol}$$

Adding HCl(aq) does not affect this equality. After the correct amount of HCl(aq) has been added

$$\frac{n_{CN^-}}{n_{HCN}} = \frac{\left[CN^-\right]}{\left[HCN\right]} = 2.46$$

Combine this equation with the preceding and solve for n_{HCN}:

$$\frac{0.0320 - n_{HCN}}{n_{HCN}} = 2.46 \quad \text{from which} \quad n_{HCN} = 0.00925 \text{ mol}$$

This is the chemical amount of H_3O^+ that must be added, because each mole of H_3O^+ gives one of HCN. Then

$$V_{HCl} = \frac{0.00925 \text{ mol}}{0.100 \text{ mol L}^{-1}} = 0.0925 \text{ L} = 92.5 \text{ mL}$$

15.52 • Before any NaOH is added: $\left[H_3O^+\right]$ in the HBr solution is 0.1439 mol L^{-1} because HBr is a strong acid and so is completely ionized. The pH is 0.842.

• 1.00 mL short of the equivalent point: It is easy to verify that it requires 31.14 mL of 0.1219 M NaOH to titrate 26.38 mL of 0.1439 M HBr to the equivalence point. At 1.00 mL short of equivalence, 30.14 mL of NaOH has been added. The unreacted H_3O^+ comprises 0.122 mmol (the difference between the chemical amount of H_3O^+ originally present and the chemical amount of NaOH added). The volume of the solution is 26.38 mL + 30.14 mL = 56.52 mL. The concentration of the H_3O^+ is its chemical amount divided by this volume or 2.16×10^{-3} M, and the pH is 2.666.

• At the equivalence point in a strong acid/strong base titration, the pH is 7.00.

• 1.00 mL past the equivalent point: 32.14 mL of NaOH has been added, the concentration of OH^- is the chemical amount of unreacted OH^- divided by the volume of the solution. This is 0.122 mmol divided by 58.52 mL, which is 2.085×10^{-3} mol L^{-1}. The pOH is 2.681, and the pH is 14.000 -pOH or 11.319.

15.54 • The pH after 0 mL of 0.1000 M NaOH titrant has been added to 50.00 mL of a 0.1000 M solution of chloroacetic acid: the acid is a weak acid. Let $x=\left[H_3O^+\right]$

$$\frac{x^2}{0.1000-\left[H_3O^+\right]}=1.4\times10^{-3} \quad \text{from which} \quad x=\left[H_3O^+\right]=1.12\times10^{-2}\ \text{M}\ \text{pH}=1.95$$

• The pH after 5.00 mL of 0.1000 M NaOH titrant has been added:

$$\frac{\left(\left(0.500\text{ mmol}/55.00\text{ mL}\right)+x\right)x}{\left(4.50\text{ mmol}/55.00\text{ mL}\right)-x}=\frac{\left(9.091\times10^{-3}+x\right)x}{8.182\times10^{-2}-x}=1.4\times10^{-3}$$

$$x^2+1.049\times10^{-2}x-1.145\times10^{-4}=0 \quad x=\left[H_3O^+\right]=6.67\times10^{-3} \quad \text{pH}=2.18$$

• The pH after 25.00 mL of titrant has been added:

$$\frac{\left(\left(2.50\text{ mmol}/75.00\text{ mL}\right)+x\right)x}{\left(2.50\text{ mmol}/75.00\text{ mL}\right)-x}=\frac{\left(0.0333+x\right)x}{0.0333-x}=1.4\times10^{-3}$$

$$x=\left[H_3O^+\right]=1.3\times10^{-3} \quad \text{pH}=2.89$$

• The pH after 49.00 mL of titrant has been added:

$$\frac{\left(\left(4.90\text{ mmol}/99.00\text{ mL}\right)+x\right)x}{\left(0.10\text{ mmol}/99.00\text{ mL}\right)-x}=1.4\times10^{-3}$$

$$x=\left[H_3O^+\right]=2.8\times10^{-5} \quad \text{pH}=4.56$$

• The pH after 49.90 mL of titrant has been added:

$$\frac{\left(\left(4.99\ \text{mmol}/99.90\ \text{mL}\right)+x\right)x}{\left(0.010\ \text{mmol}/99.90\ \text{mL}\right)-x}=1.4\times10^{-3}$$

$$x=\left[H_3O^+\right]=2.7\times10^{-6}\quad \text{pH}=5.56$$

• The pH after 50.00 mL of titrant has been added, the equivalence point: the system contains 0.0500 M sodium chloroacetate ($NaClCH_2COO$). The anion hydrolyzes

$$ClCH_2OO^-(aq)+H_2O(l)\rightleftharpoons ClCH_2COOH(aq)+OH^-(aq)$$

$$\left[CH_2ClCOOH\right]=\left[OH^-\right]=y$$

$$\frac{y^2}{0.0500-y}=K_b=\frac{1.0\times10^{-14}}{1.4\times10^{-3}}=7.14\times10^{-12}$$

$$y=\left[OH^-\right]=6.0\times10^{-7}\quad \text{pOH}=6.22\quad \text{pH}=7.78$$

• The pH after 50.10 mL of titrant has been added (0.10 mL NaOH beyond the equivalence point):

$$\left[OH^-\right]=\frac{(0.10\ \text{mL})(0.1000\ \text{M})}{100.10\ \text{mL}}=1.0\times10^{-4}\ \text{M}\quad \text{pOH}=4.00\quad \text{pH}=10.00$$

The pH after 55.00 mL of titrant has been added:

$$\left[OH^-\right]=\frac{(5.00\ \text{mL})(0.1000\ \text{M})}{105.00\ \text{mL}}=4.76\times10^{-3}\ \text{M}\quad \text{pOH}=2.32\quad \text{pH}=11.68$$

15.56 The original solution (before any titrating acid is added) is 0.175 M aqueous NH_3. Ammonia acts as a base in water

$$NH_3(aq)+H_2O(l)\rightleftharpoons NH_4^+(aq)+OH^-(aq)\qquad \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}=K_b=1.8\times10^{-5}$$

If the equilibrium concentration of NH_4^+ is *x*, then the equilibrium concentration of NH_3 is 0.175 - *x*; and that of OH^- is *x*. The other sources of OH^- are negligible. Substitution and solving for *x* (by iteration) gives $\left[OH^-\right]=1.766\times10^{-3}$ M and a pH of 11.25.

Text section 15.6 shows that in the titration of a weak acid with a strong base, the pH at the half-equivalence point is very close to the pK_a of the weak acid: pK_a = pH. Construct the analogous relationship $pK_b=\text{pOH}$ to apply to the titration of a weak base with a strong acid. Then, pH = 14.00 - pOH = 14.00 - 4.745 = 9.26

It requires (0.175/0.106) (140.0) = 231.13 mL to titrate the solution to the equivalence point, at which point the total volume of the solution is 371.13 mL. The solution is in effect dilute aqueous NH_4Cl in which the concentration of the NH_4^+ ion is nominally 0.175(140.00/371.13) = 0.0660 M. This concentration is lowered slightly by the reaction of the NH_4^+ ion with water to generate H_3O^+ and NH_3. The K_a for this reaction is

$$\frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

Substituting in the usual way into the equilibrium expression for this acid ionization gives $\left[H_3O^+\right] = 6.06\times10^{-6}$ M, pH = 5.22.

When the titration is 1.00 mL past the equivalence point, the NH_4^+ is still present but is completely overshadowed as a source of H_3O^+ by the excess HCl(*aq*). Consider only the HCl. The first 231.13 mL of 0.106 M HCl were neutralized, so the effective concentration of HCl in the solution is the amount of HCl contributed by the last 1.00 mL divided by the total volume of the solution. This is $\left(1.00/372.13\right)\left(0.106\right) = 2.85\times10^{-4}$ M. This is also the concentration of H_3O^+ so the pH is 3.55.

15.58 The total chemical amount of HCl added is 18.393 mmol; the total chemical amount of NaOH added is 7.917 mmol. These numbers, which come from multiplying the concentrations of the acid and base by their respective total volumes in mL, are not equal. The tablet supplies the base needed to neutralize 18.393 - 7.917 = 10.476 mmol of H_3O^+. The reaction is

$$CaCO_3(s) + 2H_3O^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + 3H_2O(l)$$

Each mole of $CaCO_3$ takes up 2 mol of H_3O^+ so there is in the tablet ((10.476/2) = 5.238) mmol of $CaCO_3$. The molar mass of $CaCO_3$ is 100.09 g mol^{-1} so the tablet contains 0.5243 g of $CaCO_3$. This is 39.54% of its total mass.

15.60 At the end-point of her titration, the chemist has a solution of $NH_4^+(aq)$ ion that is about 0.050 M. This Brønsted-Lowry acid makes the solution acidic

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

The K_a for this equilibrium is 5.6×10^{-10}. Let x equal the equilibrium concentration of the H_3O^+ and NH_3. Then

$$5.6\times10^{-10} = \frac{x^2}{0.050 - x}$$

The x in this equation is about 5.3×10^{-6} so the pH is about 5.3. An appropriate indicator would be methyl red.

15.62 The concentration of the cacodylate ion in the original solution is 0.1000 M. A 50.00 mL aliquot of this solution contains 0.005000 mol of cacodylate ion; 29.55 mL of 0.100 M HCl contains 0.002955 mol of HCl. When the HCl is added to the aliquot it generates 0.002955 mol of cacodylic acid. Some cacodylate ion, 0.005000 - 0.002955 = 0.002045 mol, is left in excess. The equilibrium expression for the acid ionization of cacodylic acid is

$$\frac{\left[\text{cacodylate}\right]\left[H_3O^+\right]}{\left[\text{cacodylate acid}\right]} = K_a$$

All the quantities on the left are known:

$$\left[\text{cacodylate}\right] = \frac{0.002045}{0.07955}\text{M} \quad \left[\text{cacodylate acid}\right] = \frac{0.002955}{0.07955}\text{M} \quad \left[H_3O^+\right] = 1.0\times10^{-6}\text{ M}$$

Substitution gives $K_a = 6.9\times10^{-7}$.

15.64 The successive equilibrium constants for the two-step ionization of phthalic acid differ by a factor of several thousand. Because the amounts of HPh^- and H_3O^+ produced by the first step are far larger than the amount consumed (in the case of HPh^-) or produced (in the case of H_3O^+) by the second step, the steps may be considered separately. Also, the autoionization of water is a negligible source of H_3O^+ in this solution. The first stage in the ionization provides the expression

$$\frac{[H_3O^+][HPh^-]}{[H_2Ph]} = K_{a1} = 1.26\times10^{-3} = \frac{x^2}{0.0100 - x}$$

where x is the equilibrium concentration of H_3O^+. Solving the resulting equation gives $x = 2.98\times10^{-3}$. The equilibrium concentrations of HPh^- and H_3O^+ are 2.98×10^{-3} M. That of H_2Ph is $0.0100 - x = 0.0070$ M.

The second stage of ionization is governed by the expression

$$\frac{[H_3O^+][Ph^{2-}]}{[HPh^-]} = K_{a2} = 3.10\times10^{-6} = \frac{y(2.98\times10^{-3})}{2.98\times10^{-3}}$$

where y is the equilibrium concentration of the Ph^{2-} ion. $[Ph^{2-}] = 3.10\times10^{-6}$ M.

15.66 This problem resembles problem **15.64** in that it treats a two-stage process in which the successive equilibrium constants differ so greatly that the stages can be treated separately. Now however, a weak base, the oxalate ion, is in solution. It reacts according to the equations

$$C_2O_4^{2-}(aq) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + OH^-(aq) \quad K_{b1} = K_w/K_{a2}$$
$$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons H_2C_2O_4(aq) + OH^-(aq) \quad K_{b2} = K_w/K_{a1}$$

Let the final concentration of $HC_2O_4^-$ equal y. This is also the final concentration of OH^- because the first reaction is the only important source of OH^-. The concentration of $C_2O_4^{2-}$ ion at equilibrium is then 0.10 – y. Therefore

$$\frac{y^2}{0.10 - y} = \frac{K_w}{K_{a2}} = \frac{1.0\times10^{-14}}{6.4\times10^{-5}}$$

Thus, $y = 4.0\times10^{-6}$, and $[OH^-] = [HC_2O_4^-] = 4.0\times10^{-6}$ M. The hydrogen oxalate ion $(HC_2O_4^-)$ itself can serve as a weak base, as represented in the second chemical equation above. For that equation

$$\frac{[OH^-][H_2C_2O_4]}{[HC_2O_4^-]} = K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.0\times10^{-14}}{5.9\times10^{-2}}$$

Insertion of the known equilibrium concentrations of OH^- and $HC_2O_4^-$ gives $[H_2C_2O_4] = 1.7\times10^{-13}$ M.

At the moment of mixing, the concentration of the oxalate ion was 0.10 M. Some of this oxalate then reacted, but not much—there is only a tiny concentration of hydrogen oxalate ion

$(4.0\times10^{-6}\text{ M})$ and an incredibly tiny concentration of oxalic acid $(1.7\times10^{-13}\text{ M})$. The final concentration of oxalate ion is still 0.10 M.

15.68 Dissolved carbonates are in the rain drop as either carbonic acid, hydrogen carbonate ion or carbonate ion:

$$3.6\times10^{-5} = [H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]$$

where all of the quantities on the right are to be determined. The existence of the acid ionization equilibria of carbonic acid provides additional relationships among these quantities:

$$\frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = K_{a1} = 4.3\times10^{-7} \qquad \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = K_{a2} = 4.8\times10^{-11}$$

The $[H_3O^+]$ is 1.0×10^{-4} M in these equations. The upshot is three equations in three unknowns. The easiest way to solve this system of equations is to observe that $[CO_3^{2-}]$ is likely to be quite small—almost all of the dissolved carbonate is tied up with hydrogen ion because hydrogen ion is abundant in this acidic solution. Setting $[CO_3^{2-}]$ to zero gives:

$$3.6\times10^{-5} \approx [H_2CO_3]+[HCO_3^-]$$

$$\frac{[HCO_3^-](1.0\times10^{-4})}{[H_2CO_3]} \approx 4.3\times10^{-7}$$

Solving this pair of simultaneous equations gives

$$H_2CO_3 = 3.6\times10^{-5}\text{M} \quad \text{and} \quad [HCO_3^-] = 1.55\times10^{-7}\ m$$

Now, substitution in the K_{a2} expression gives $[CO_3^{2-}] = 7.4\times10^{-14}$ M. Almost all of the carbonate is present as carbonic acid, a small amount is present as hydrogen carbonate ion, and a vanishingly tiny fraction is present as CO_3^{2-} ion.

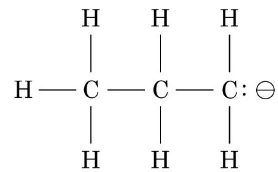
15.70 Compare the pK_a of methane (given as 49 in text Table 15.4) to that of nitromethane (given as 10.2). Use the approach of text Example 15.16

$$\begin{aligned}\Delta G^\circ - \Delta G^{\circ\prime} &= 2.3RT(\text{p}K_a - \text{p}K_a^{\prime})\\ &= 2.3(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})(10.2-49)\\ &= -2.2\times10^{5}\text{ J mol}^{-1}\end{aligned}$$

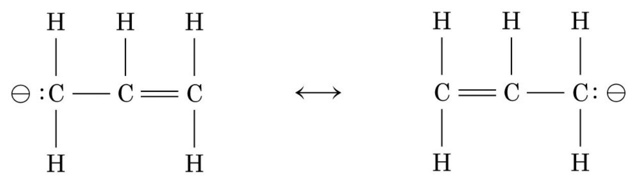
The stabilization offered by the nitro group is 220 kJ mol^{-1}.

15.72 In each case, the hydrogen is attached to an atom X (=O, C, N) that is bonded to an R-C=O group. The critical difference is the electronegativity of X. Because oxygen is the most electronegative of the three, RCOOH should be the strongest acid and have the lowest pK_a. Carbon is the least electronegative, so $RCOCH_3$ will have the highest pK_a. The amide, $RCONH_2$, will be in between.

15.74 The conjugate base of propane has a single Lewis structure:



The conjugate base of propene has two resonance Lewis structures:



Resonance stabilization makes propene the stronger acid because it gives it a more stable conjugate base.

15.76 **a)** Propionic acid $\left(CH_3CH_2COOH\right)$ will be the stronger acid since its conjugate base is less sterically hindered and thus more stable (better solvated) in aqueous solution.

b) Trichloroacetic acid $\left(CCl_3COOH\right)$ will be the stronger acid since Cl is more electronegative than I, thus stabilizing the negative charge on the conjugate base.

c) 2-chlorobutanoic acid $\left(CH_3CH_2CHClCOOH\right)$ will be the stronger acid since the Cl is closer to the negatively charged —COO$^-$ end group of the conjugate base, stabilizing it.

15.78 Figure out the original concentration of the acetic acid

$$c_a = \frac{40.0 \text{ g L}^{-1}}{60.05 \text{ g mol}^{-1}} = 0.666 \text{ M}$$

The million-to-one dilution reduces this concentration to $c_a = 6.66\times10^{-7}$ M. Substitute in the cubic equation in text Section 15.8 with c_b equal to zero

$$\left[H_3O^+\right]^3 + K_a\left[H_3O^+\right]^2 - \left(K_w + c_aK_a\right)\left[H_3O^+\right] - K_aK_w = 0$$

$$\left[H_3O^+\right]^3 + 1.76\times10^{-5}\left[H_3O^+\right]^2 - 1.173\times10^{-11}\left[H_3O^+\right] - 1.76\times10^{-19} = 0$$

A scientific calculator quickly gives the roots of this equation

$$\left[H_3O^+\right] = -1.824\times10^{-5},\quad 6.572\times10^{-7},\quad -1.468\times10^{-8}$$

The physically correct answer cannot be negative. This eliminates the first and third roots.

$$\left[H_3O^+\right] = 6.57\times10^{-7} \text{ M} \quad \text{pH} = 6.18$$

The equation can also be solved by choosing a series of values for $[H_3O^+]$ and finding where the function passes through zero (see text Appendix C).

15.80 **a)** Let Q stand for quinine $\left(C_{20}H_{24}O_2N_2\right)$ and HQ^+ for the conjugate acid of quinine. The molar mass of Q is 324.4 g mol^{-1}. Q reacts with water as a base

$$Q + H_2O \rightleftharpoons HQ^+ + OH^- \qquad K_{b1} = 3.31\times10^{-6}$$
$$HQ^+ + H_2O \rightleftharpoons H_2Q^{2+} + OH^- \qquad K_{b2} = 1.35\times10^{-10}$$

The concentration of the original solution of Q is

$$c_Q = \frac{1.622\ \text{g}}{\left(324.4\ \text{g mol}^{-1}\right)\left(0.10000\ \text{L}\right)} = 0.05000\ \text{mol L}^{-1}$$

• When 0 ml of 0.1000 M HCl has been added:

$$x = \left[OH^-\right] = \left[HQ^+\right]$$
$$\frac{x^2}{0.05000 - x} = 3.31\times10^{-6} \qquad x = 4.05\times10^{-4}\ \text{mol L}^{-1}$$
$$\left[H_3O^+\right] = \frac{1.00\times10^{-14}}{4.05\times10^{-4}} = 2.47\times10^{-11}\ \text{mol L}^{-1} \qquad \text{pH=10.61}$$

• After 25.00 ml of 0.1000 M HCl has been added: $[Q]_0 = [HQ^+]_0 = 0.0200$

$$\frac{\left[HQ^+\right]\left[OH^-\right]}{\left[Q\right]} = \frac{\left(0.0200 + x\right)x}{0.0200 - x} = 3.31\times10^{-6} \qquad x = \left[OH^-\right] = 3.31\times10^{-6} \qquad \text{pH} = 8.52$$

• After 50.00 mL of 0.1000 M HCl has been added: Exactly enough acid has been added to convert all of the Q to HQ^+. The solution is a 0.0333 M solution of HQCl. The HQ^+ ion can react both as an acid and as a base. Use the equations developed in the text for treating such amphoteric equilibria

$$K_{a1} = K_w / K_{b2} = 7.41\times10^{-5} << \left[HQ^+\right] = 0.0333$$
$$K_{a2} = K_w / K_{b1} = 3.02\times10^{-9}; \quad K_{a2}\left[HQ^+\right] = 1.0\times10^{-10} >> K_w$$

Substitute in the approximate equation obtained in text Section 15.8

$$\text{pH} = \tfrac{1}{2}\left(\text{p}K_{a1} + \text{p}K_{a2}\right) = \tfrac{1}{2}\left(4.13 + 8.52\right) = 6.32$$

• After 75.00 ml of 0.1000 M HCl has been added: Focus on the second stage of ionization of Q. $V = 175$ mL, and

$$\left[HQ^+\right]_0 = \left[H_2Q^{2+}\right]_0 \frac{2.50\ \text{mmol}}{175\ \text{mL}} = 0.0143\ \text{mol L}^{-1}$$

$$\frac{\left(0.0143 + x\right)x}{0.0143 - x} = 1.35\times10^{-10} \qquad x = \left[OH^-\right] = 1.35\times10^{-10}\ \text{mol L}^{-1} \qquad \text{pH} = 4.13$$

• After 99.90 mL of 0.1000 M HCl has been added:

$$\left[H_2Q^+\right]_0 = 0.05000 \text{ mol L}^{-1} \times \frac{99.90 \text{ mL}}{199.90 \text{ mL}} = 2.499 \times 10^{-2} \text{ mol L}^{-1}$$

$$\left[HQ^+\right]_0 = 0.05000 \text{ mol L}^{-1} \times \frac{0.10 \text{ mL}}{199.90 \text{ mL}} = 2.5 \times 10^{-5} \text{ mol L}^{-1}$$

$$H_2Q^{2+} + H_2O \rightleftharpoons HQ^+ + H_3O^+$$

$$\frac{\left(2.5\times10^{-5} + x\right)x}{2.499\times10^{-2} - x} = \frac{K_w}{K_{b2}} = 7.41\times10^{-5}$$

Solve using the quadratic formula

$$x = \left[H_3O^+\right] = 1.31\times10^{-3} \quad \text{pH} = 2.88$$

• After 100.00 mL of 0.1000 M HCl has been added:

$$\left[H_2Q^{2+}\right] = 0.0250 - x$$

$$H_2Q^{2+} + H_2O \rightleftharpoons HQ^+ + H_3O^+$$

$$\frac{x^2}{0.0250 - x} = \frac{1.00\times10^{-14}}{1.35\times10^{-10}} = 7.41\times10^{-5}$$

$$x = 1.32\times10^{-3} \text{ mol L}^{-1} \quad \text{pH} = 2.88$$

• After 105.00 mL of 0.1000 M HCl has been added:

$$\left[H_3O^+\right]_0 = \frac{5.00 \text{ mL} \times 0.1000}{205.00 \text{ mL}} = 2.44\times10^{-3} \text{ M}$$

$$\left[H_3O^+\right] = 2.44\times10^{-3} + x; \left[H_2^+\right] = x; \left[H_2Q^{2+}\right] = 0.0500\left(\frac{100.00}{205.00}\right) - x$$

$$\frac{x\left(2.44\times10^{-3} + x\right)}{\left(2.44\times10^{-2} - x\right)} = 7.41\times10^{-5}$$

$$x = 5.8\times10^{-4}; \quad \left[H_3O^+\right] = 3.02\times10^{-3} \text{ mol L}^{-1} \quad \text{pH} = 2.52$$

15.82 If HX were a strong acid, it would be completely dissociated into ions in solution. Increasing its concentration by a factor of 100 would increase the conductivity by a factor of 100. If HX were a very weak acid, increasing the concentration by a factor of 100 would decrease its degree of dissociation by a factor of 10. Consequently the conductivity, would fall by a factor of only 10. The observed drop in conductivity (by a factor of 11) indicates that HX is intermediate in its strength. Let c stand for the concentration of H_3O^+ in the more dilute solution. Then

$$c = \left[H_3O^+\right] = \left[X^-\right] \text{ in 0.0010 M HX}$$

$$11\,c = \left[H_3O^+\right] = \left[X^-\right] \text{ in 0.010 M HX}$$

The same acid-ionization equilibrium exists in both solutions and thus

$$\frac{c^2}{0.0010 - c} = K \quad \text{and} \quad \frac{\left(11\,c\right)^2}{0.10 - 11\,c} = K$$

Eliminating K between the two equations and solving gives $c = 1.9\times10^{-4}$ mol L^{-1}. Obtain K by substituting this result into either equilibrium expression

$$K = \frac{\left(1.9\times10^{-4}\right)^2}{\left(0.0010 - 1.9\times10^{-4}\right)} = 4.5\times10^{-5}$$

15.84 **a)** Substitute the givens into the van't Hoff equation

$$\ln\left(\frac{K_{333}}{K_{273}}\right) = \ln\left(\frac{9.614\times10^{-14}}{1.138\times10^{-15}}\right) = \frac{-\Delta H°}{8.3145 \text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{333.15 \text{ K}} - \frac{1}{273.15 \text{ K}}\right)$$

Computation gives $\Delta H° = 56$ kJ mol^{-1}. For comparison, ΔH°_{298} computed using data from text Appendix D is 55.84 kJ mol^{-1}.

b)

$$\Delta G^{\circ}_{273} = -RT \ln K_{273} = -\left(8.3145 \text{ J K}^{-1}\text{ mol}^{-1}\right)\left(273.15 \text{ K}\right)\ln\left(1.139\times10^{-15}\right)$$
$$= 78146 \text{ J mol}^{-1}$$
$$\Delta S^{\circ} = \frac{\left(\Delta H^{\circ} - \Delta G^{\circ}_{273}\right)}{T} = \frac{\left(55840 - 78146\right)\text{J mol}^{-1}}{273.15\text{K}}$$
$$= -81.66 \text{ J K}^{-1}\text{ mol}^{-1}$$

c) The pH of water is exactly 7.00 when K_W equals exactly 1.00 × 10^{-14}. Substitute in the expression

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

to obtain

$$\ln\left(1.00\times10^{-14}\right) = -\frac{55.84\times10^{3}\text{J mol}}{8.3145\text{J K}^{-1}\text{mol}}\left(\frac{1}{T}\right) + \frac{-81.66 \text{ J K}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1}}$$

Solving for T gives the desired temperature as 299.6 K.

15.86 The correct answer is choice c. The solution of $Ca(OH)_2$ in choice c is so dilute that it is essentially indistinguishable from pure water, which has a pH of 7.00 (assuming 25°C).

15.88 The equation given in the problem is the sum of the chemical equations for the second and third acid ionizations of phosphoric acid added to two times the reverse of the equation for the second ionization of carbonic acid. Hence, the desired equilibrium constant is

$$K = \frac{K_{a2,H_3PO_4} K_{a3,H_3PO_4}}{\left(K_{a3,H_2CO_3}\right)^2} = \frac{\left(6.23\times10^{-8}\right)\left(2.2\times10^{-13}\right)}{\left(4.8\times10^{-11}\right)^2} = 5.9$$

15.90 Strength:

$$OP\left(OH\right)_3 \approx O_2P_2\left(OH\right)_4 < O_3P_2\left(OH\right)_4 < O_5P_3\left(OH\right)_5 < O_6P_3\left(OH\right)_3$$

The formulas have been re-written to highlight the ratio of the number of lone oxygen atoms to phosphorus atoms.

15.92 The solution of the weak acid, acetic acid, and the solution of the strong acid, hydrochloric acid, have the same pH, according to the color of the indicator. Because acetic acid is weak, its concentration in solution must be greater than the concentration of a strong acid to bring the pH down to a particular value. The solution of acetic acid contains more moles of acid, so it can neutralize more moles of base.

15.94 The K_a of HF (6.6×10^{-4}) is 22 000 times larger than the K_a of HClO (3.0×10^{-8}). It is so much stronger as an acid that it determines the pH in any solution containing comparable concentrations of the two. The initial concentration is $[HF]_0$ = 0.23 mol/3.60 L = 0.0639 mol L^{-1}. Set $x = [H_3O^+] = [F^-]$ and substitute in the equilibrium expression

$$\frac{x^2}{0.0639 - x} = K_a = 6.6 \times 10^{-4}$$

Solving using this quadratic formulas gives $x = 6.17 \times 10^{-3} = [H_3O^+]$ for a pH of 2.21. Also

$$[F^-] = 6.17 \times 10^{-3} \quad [HF] = 0.0639 - x = 0.058$$

Essentially all the HClO remains un-ionized. The relevant concentrations are

$$\left[HClO\right] = \frac{0.57 \text{ moI}}{3.60 \text{ L}} = 0.16 \text{ mol L}^{-1} \quad \left[ClO^-\right] = \frac{K_a\left[HClO\right]}{\left[H_3O^+\right]} = 7.7 \times 10^{-7} \text{mol}^{-1}$$

15.96 Combine the two equations by subtracting the second from the first

$$NH_4^+ + CN \rightleftharpoons NH_3 + HCN \quad \frac{\left[NH_3\right]\left[HCN\right]}{\left[NH_4^+\right]\left[CN^-\right]} = \frac{5.6 \times 10^{-10}}{6.17 \times 10^{-10}} = 0.9076$$

At equilibrium in this reaction $[NH_3] = [HCN] = x$ and $\left[NH_4^+\right] = \left[CN^-\right] = 0.100 - x$. In writing this, the assumption is that $[H_3O^+]$ and $[OH^-] << [NH_3]$ and [HCN]. Use the equilibrium constant expression to solve for the unknown

$$\frac{x^2}{(0.100 - x)^2} = 0.9076 \text{ from which } \frac{x}{0.100 - x} = 0.9527 \text{ from which } x = 0.0488$$

Use this result in the K_a expression for ammonium ion to obtain $[H_3O^+]$

$$\left[H_3O^+\right] = \frac{NH_4^+}{[NH_3]} K_a = \frac{0.100 - 0.0488}{0.0488}\left(5.6 \times 10^{-10}\right) = 5.9 \times 10^{-10}$$

The same answer is obtained using the HCN / CN^- equilibrium with the K_a for HCN.

15.98 At pH 6.0, $[H_3O^+] = 1.0 \times 10^{-6}$ M, so

$$\frac{\left[Z^{2-}\right]}{\left[HZ-\right]} = \frac{K_2}{\left[H_3O^+\right]} = \frac{5 \times 10^{-7}}{1.0 \times 10^{-6}} = 0.5$$

To raise the pH of the solution of the acid H_2Z up to 6.0, you must convert all of it to the first conjugate base HZ^- and then convert 1/3 of the HZ^- on to *its* conjugate base Z^{2-}. Doing this fixes the ratio in the preceding equation to the required value

$$\frac{[Z^{2-}]}{[HZ^-]} = \frac{1/3}{2/3} = \frac{1}{2}$$

Add 4/3 mol of OH^- ion for every mole of H_2Z initially present. You have 1.0 L of 1.0 M H_2Z. Add 1333 mL of 1.0 M NaOH.

15.100 At pH 10.00, $[H_3O^+] = 1.0 \times 10^{-10}$. Consequently

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{K_{a2}}{[H_3O^+]} = \frac{4.8\times10^{-11}}{1.0\times10^{-10}} = 0.48$$

$$[CO_3^{2-}] = 0.48[HCO_3^-] \quad n_{CO_3^{2-}} = 0.48 n_{HCO_3^-} \quad n_{Na_2CO_3} = 0.48\ n_{NaHCO_3}$$

Compute the masses of the two substances that give these relationships

$$0.48\ n_{NaHCO_3}(105.99\ \text{g mol}^{-1}) + n_{NaHCO_3}(84.01\ \text{g mol}^{-1}) = 10.0\ \text{g}$$

$$n_{NaHCO_3} = 7.41\times10^{-2}\ \text{mol}$$

$$m_{NaHCO_3} = 6.23\ \text{g} \quad m_{Na_2CO_3} = 3.77\ \text{g}$$

$$x = 1.05\times10^{-4} = [H_3O^+] \quad \text{so that} \quad \text{pH} = 3.98$$

15.102 The pH shoots up suddenly upon the addition of 0.02 mL of sodium hydroxide solution. This is the indication of an end-point; thus 4.71 + 0.02 = 4.73 mL of 0.0410 M NaOH is just enough to bring the titration to the first equivalence point. At the end-point, the chemical amount of base that has been added equals the chemical amount of phosphoric acid that was present. The chemical amount of base is (0.0410 mol L^{-1} × 0.00473 L). This is therefore also the chemical amount of acid. The original concentration of the phosphoric acid equals this amount divided by 0.05000 L (50.00 mL) or 3.88×10^{-3} mol L^{-1}.

15.104 **a)** $Na_2CO_3 + 2\ HA \rightarrow CO_2 + \text{other products}$

$$n_{CO_3^{2-}} = \tfrac{1}{2} n_{HA} = \tfrac{1}{2}(40.0\ \text{mL})(0.50\ \text{mmol mL}^{-1}) = 10\ \text{mmol}$$

$$c_{CO_3^{2-}} = \frac{10\ \text{mmol}}{20.0\ \text{mL}} = 0.50\ \text{mol L}^{-1}$$

b) Consider 1 L of solution. The mass of solute is

$$m_{Na_2CO_3} = 0.50\ \text{mol} \times 106\ \text{g mol}^{-1} = 53\ \text{g}\ Na_2CO_3$$

The solute is 5.0% of the whole mass, so the mass of the 1 L of solution is 53 g/0.050 = 1060 g. The density of the solution is 1.06 g mL^{-1} or, to two significant figures, 1.1 g mL^{-1}.

c) $m = 53\ \text{g} \times (286.2\ \text{g mol}^{-1}/106.0\ \text{g mol}^{-1}) = 143\ \text{g}\ Na_2CO_3 \cdot 10H_2O$.

15.106 **a)** Let $x = [OH^-]$. Then

$$7\times10^{-6} = \frac{x^2}{(0.0200 - x)} \quad \text{which leads to } x = 4\times10^{4}\text{mol L}^{-1}$$

The pOH is - log(4 × 10^{-4}) = 3.4, so the pH is 10.6.

b) At the equivalence point the system is a 0.010 M solution of the conjugate acid of Novocain, for which

$$K_a = \frac{K_W}{(7\times10^{-6})} = 1.4\times10^{-9}$$

Let $y = [H_3O^+]$ in this solution. Then

$$1.4\times10^{-9} = \frac{y^2}{(0.010-y)} \quad \text{so that} \quad y = 4\times10^{-6} = \left[H_3O^+\right]$$

At the equivalence point pH = 5.4.

15.108 The vinegar under analysis contains around 5 g of acetic acid per 100 g. Acetic acid is CH_3COOH ($\mathcal{M}$ = 60.05 g mol^{-1}). If the density of the vinegar is 1.0 g cm^{-3}, then Anne Dalton proposes to titrate 50.00 mL samples of about 0.83 M acetic acid. Using 1.000 M NaOH she can expect to need around 42 mL of base for each titration. If she detects the equivalence point to within ±0.02 mL, then her precision is $(\pm0.02/42)100 \approx 0.05\%$. Charlie Cannizzaro's method of analysis would give an uncertainty of ±0.01 in the pH and therefore an uncertainty of $10^{\pm0.01}$ in the concentration of H_3O^+. Because 10 raised to the 0.01 power is 1.023, this means that Charlie's result for the hydronium ion concentration would have ±2.3% uncertainty. The same uncertainty attaches to $[CH_3COO^-]$, which is equal to $[H_3O^+]$. Using the K_a expression to solve for the acetic acid concentration gives a total uncertainty of about 4.6%. Anne Dalton's method is more precise. Its drawback is that it is slower and requires more skill. Anne Dalton gets hired.

15.110 The exhalation of the $CO_2(g)$ through the shell of the egg should lead to a rise in the pH of the contents—a weak acid is being lost from the system.

15.112 The formula of the hydrogen tartrate anion is $HC_4H_4O_6^-$. The dissolution of potassium hydrogen tartrate gives this ion along with potassium ions. Hydrogen tartrate ion acts as a base in the reaction:

$$HC_4H_4O_6^-(aq) + H_3O+(\text{aq}) \rightleftharpoons H_2C_4H_4O_6(aq) + H_2O(l)$$

to counteract the effect of an added acid and as an acid in the reaction:

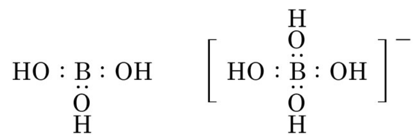
$$HC_4H_4O_6^-(aq) + OH^-(aq) \rightleftharpoons C_4H_4O_6^{2-}(aq) + H_2O(l)$$

to counteract the effect of an added base.

15.114 The conjugate acid of a tertiary amine R_3N has the formula R_3NH^+. The bulk of the R groups in such an ion impairs its interaction with the solvent (water) compared to H_3NH^+, which is the conjugate acid of NH_3. On the basis of steric effects, a tertiary amine R_3N should be a weaker base than ammonia.

15.116 The equilibrium constant K_w for the autoionization of water increases with increasing temperature. By LeChâtelier's principle, this reaction must be endothermic.

15.118 **a)** $B(OH)_3$ is a Lewis acid that accepts an electron pair from OH^-. The acid-base interaction gives the adduct $B(OH)_4^-$ which is itself capable of serving further as a Lewis base (electron-pair donor).



b) Let $x = \left[B(OH)_4^-\right] = \left[H_3O^+\right]$

$$\frac{x^2}{0.20 - x} = K_a = 5.8\times10^{-10}$$

$$x = 1.1\times10^{-5} = \left[H_3O^+\right] \quad \text{so that} \quad \text{pH} = 4.97$$

15.120 Assume that the pressure of $CO_2(g)$ over the solution equals the local (Denver) atmospheric pressure and use Henry's law

$$X_{CO_2} = \frac{P_{CO_2}}{k} = \frac{0.833 \text{ atm}}{1.8\times10^3 \text{ atm}} = 4.63\times10^{-4}$$

One liter of water contains 55.5 mol water. The chemical amount of dissolved CO_2 is

$$\frac{n_{CO_2}}{n_{CO_2} + 55.5 \text{ mol}} = X_{CO_2} = 4.63\times10^{-4}$$

Solving gives $n_{CO_2} = 0.0257$ mol, so $[CO_2]_0$ = 0.0257 M = $[H_2CO_3]_0$. The pH for the diprotic acid is determined by the first acid dissociation. Let

$$x = \left[HCO_3^-\right] = \left[H_3O^+\right]$$

Then

$$\frac{x^2}{0.0257 - x} = K_{a1} = 4.3\times10^{-7}$$

$$x = 1.05\times10^{-4} = \left[H_3O^+\right] \quad \text{so that} \quad \text{pH} = 3.98$$

Chapter 16

Solubility and Precipitation Equilibria

16.2 Even "bone-dry" residues can contain chemically bound water of crystallization. The 1.00 g sample of $MgSO_4$ amounts to 8.308×10^{-3} mol. It picks up 0.898 g of H_2O when the solution is evaporated in one temperature range but only 0.150 g of H_2O when the solution is evaporated in the second temperature range. These amounts are 0.0498 and 0.00833 mol. The chemical amount of H_2O associated in the solid is 6.00 times the chemical amount of $MgSO_4$ in the first case and 1.00 times the chemical amount of $MgSO_4$ in the second case. The two formulas therefore are $MgSO_4 \cdot 6H_2O$ and $MgSO_4 \cdot H_2O$.

16.4 The 255 g of $AgNO_3$ is 1.50 mol of $AgNO_3$. The dissolution of this much $AgNO_3$ in 100 g of water is just like the dissolution of 15.0 mol of silver nitrate in 1.00 kg of water. The graph in text Figure 16.3 shows that 1.00 kg of water at 95°C easily accommodates 15.0 mol of $AgNO_3$, but that cooling the solution to about 30°C causes $AgNO_3(s)$ to tend to precipitate.

16.6 $Pb_3(SbO_4)_2(s) \rightleftharpoons 3\ Pb^{2+}(aq) + 2\ SbO_4^{3-}(aq) \quad [Pb^{2+}]^3[SbO_4^{3-}]^2 = K_{sp}$

16.8 The dissolution reaction and solubility-product expression are

$$TlSCN(s) \rightleftharpoons Tl^{+}(aq) + SCN^{-}(aq) \quad [Tl^{+}][SCN^{-}] = K_{sp} = 1.82 \times 10^{-4}$$

If neither of the ions reacts significantly with the solvent or each other to form other species at 25°C, then the concentrations of the two are equal at equilibrium and

$$[Tl^{+}] = [SCN^{-}] = \sqrt{1.82 \times 10^{-4}} = 1.35 \times 10^{-2}\ \text{mol L}^{-1}$$

The molar mass of T1SCN is 262.47 g mol^{-1} so 3.54 g of it dissolves per liter of solution, or 0.354 g per 100 mL.

16.10 $(NH_4)_2(PtCl_6)(s) \rightleftharpoons 2\ NH_4^+(aq) + PtCl_6^{2-}(aq) \quad [NH_4^+]^2[PtCl_6^{2-}] = K_{sp} = 5.6\times10^{-6}$. Let $S = [PtCl_6^{2-}]$ at equilibrium at 20°C. If neither of the product ions reacts significantly with the solvent or with each other, then at equilibrium $[NH_4^+] = 2S$. Substitution gives

$$(2S)^2 S = 5.6\times10^{-6} \text{ which is easily solved: } S = 0.011 \text{ mol L}^{-1}$$

The gram solubility is (0.011 mol L^{-1})(443.87 g mol^{-1}) = 5.0 g L^{-1}.

16.12 $Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq) \quad [Hg_2^{2+}][Cl^-]^2 = K_{sp} = 2\times10^{-18}$.

If neither of the product ions reacts significantly with the solvent or with each other, 1 mol of Hg_2^{2+} ion and 2 mol of Cl^- ion appear in solution for every 1 mol of solid that dissolves. Let S equal the concentration of Hg_2^{2+} ion at equilibrium. Then the concentration of Cl^- ions is $2S$. Substitution in the K_{sp}-expression gives

$$(2S)^2S = 2\times10^{-18}$$

Solving for S gives equilibrium concentrations of 8×10^{-7} mol L^{-1} for Hg_2^{2+} (aq) and 2×10^{-6} mol L^{-1} for $Cl^-(aq)$.

16.14 The molar mass of lead(II) iodate is 557.0 g mol^{-1}. Its solubility is

$$S = \frac{0.00896\text{ g}}{0.400\text{ L}}\times\frac{1\text{ mol}}{557.0\text{ g}}\times4.02\times10^{-5}\text{ mol L}^{-1}$$

Assume that the only reaction taking place is the dissolution equilibrium:

$$Pb(IO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ IO_3^-(aq) \quad [Pb^{2+}][IO_3^-]^2 = K_{sp}$$

Then $K_{sp} = S(2S)^2$ and $K_{sp} = 2.6\times10^{-13}$.

16.16 The molar mass of $Ag_2Cr_2CO_7$ is 431.72 g mol^{-1}, so its solubility is 1.31×10^{-4} mol L^{-1}. The K_{sp} is obtained by substitution as in problem **16.14**: $K_{sp} = 9.0\times10^{-12}$.

16.18 The 0.090 g of PbI_2 ($\mathcal{M}$ = 461.0 g mol^{-1}) is 1.95×10^{-4} mol. The concentration of $Pb^{2+}(aq)$ in the hot solution is 1.95×10^{-4} mol L^{-1}; the concentration of I^- (aq) is twice this, 3.90×10^{-4} mol L^{-1}. These concentrations hardly change as the solution is cooled, but the K_{sp} of the dissolution-precipitation equilibrium does change. At 25°C, it equals 1.4×10^{-8} (see Table 16.2). Does the reaction quotient Q exceed K_{sp}?

$$Q = [Pb^{2+}][I^-]^2 = (1.95\times10^{-4})(3.90\times10^{-4})^2 = 3.0\times10^{-11}$$

This value is less than K_{sp}. No precipitate forms.

16.20 The calcium chloride and sodium fluoride solutions dilute each other as they are mixed. The concentration of Ca^{2+} is 2/3 of 0.0010 M immediately after mixing, and the concentration of F^- is 1/3 of 6.0×10^{-5} M. Substituting these concentrations in the K_{sp} expression for CaF_2 gives a Q of about 2.7×10^{-13}. Because this is less than K_{sp}, no precipitate forms.

16.22 The volume of the combined solutions is 8.10 L. After mixing but before any reaction occurs, the concentrations of the reacting ions are

$$\left[\mathrm{Ag^+}\right]=\left(\frac{1.50}{8.10}\right)\left(0.080\right)=0.0148\ \mathrm{M} \quad \text{and} \quad \left[\mathrm{I^-}\right]=\left(\frac{6.60}{8.10}\right)\left(0.10\right)=0.0815\ \mathrm{M}$$

The two ions react in a 1:1 proportion, so Ag^+ ion is the limiting reactant. At equilibrium, almost all of the Ag^+ is removed from solution as AgI(*s*). The remaining concentration of I^- (*aq*) is 0.0815 - 0.0148 = 0.0667 M. Inserting this value into the K_{sp} expression gives

$$\left[\mathrm{Ag^+}\right]\left[\mathrm{I^-}\right]=\left[\mathrm{Ag^+}\right]\left[0.0667\right]=1.5\times10^{-16}$$

Solving gives an equilibrium concentration of Ag^+ of 2.25×10^{-15} mol L^{-1}. The amounts of Ag^+ in solution before and after the mixing are

$$n_{\mathrm{Ag^+}}\left(\text{before}\right)=0.080\ \mathrm{mol^{-1}}\times1.50\ \mathrm{L}=0.12\ \mathrm{mol}$$
$$n_{\mathrm{Ag^+}}\left(\text{after}\right)=2.25\times10^{-15}\mathrm{mol\ L^{-1}}\times8.10\mathrm{L}=1.82\times10^{-14}\mathrm{mol}$$

The fraction of silver ion remaining in solution is the second of these amounts divided by the first: 1.5×10^{-13}.

16.24 The reaction responsible for the precipitate is

$$\mathrm{Sr^{2}}\left(aq\right)+2\mathrm{F^-}\left(aq\right)\rightleftharpoons\mathrm{SrF_2}\left(s\right) \quad \left[\mathrm{Sr^{2+}}\right]\left[\mathrm{F^-}\right]^2=K_{sp}=2.8\times10^{-9}$$

The chemical amount of F^- ion is 4.00 mmol, and the chemical amount of Sr^{2+} is 3.20 mmol. Imagine that all of the F^- ion reacts (it is the limiting reactant). Then 1.20 mmol of Sr^{2+} remains at a concentration of 1.20 mmol/120 mL = 0.0100 mol L^{-1}. Now, suppose that the SrF_2(s) starts to redissolve. Some Sr^{2+} comes into solution but the amount is negligible compared to the amount of unreacted excess Sr^{2+}. The dissolution of SrF_2 is however the *only* source of F^- *(aq)*. The dissolution goes to equilibrium, at which the K_{sp} relationship is satisfied. Inserting $[Sr^{2+}]$ = 0.0100 mol L^{-1} gives $[F^-] = 5.3 \times 10^{-4}$ mol L^{-1}.

16.26 The common-ion effect greatly reduces the solubility of the AgCl, which is only very slightly soluble in pure water anyway. Let S represent the solubility. Then, $[Cl^-] = (0.150 + S)$ M and $[Ag^+] = S$ M. Substituting in the K_{sp} expression gives

$$K_{sp} = [\mathrm{Ag^-}][\mathrm{Cl^-}] = S(0.150 + S) = 1.6 \times 10^{-10}$$

Solving for S gives the molar solubility of AgCl: 1.07×10^{-9} M. This means that 1.07×10^{-10} mol of AgCl dissolves in 100 mL of the 0.150 M NaCl. Multiplying by 143.3 g mol^{-1}, the molar mass of AgCl, gives a gram solubility of 1.5×10^{-8} g per 100 mL.

16.28 **a)** Let S stand for the molar solubility of the silver arsenate. From the equilibrium law for the dissolution-precipitation reaction

$$K_{sp}=1.0\times10^{-22}=\left[\mathrm{Ag^+}\right]^3\left[\mathrm{AsO_4^{3-}}\right]=\left(3S\right)^3S$$

Solving gives $S = 1.4 \times 10^{-6}$ mol L^{-1}

b) Now, use $[Ag^+]$ = 0.100 M in the equilibrium expression and let the concentration of AsO_4^{3-} equal S. Substituting and solving gives $S = 1.0 \times 10^{-19}$ mol L^{-1}.

16.30 Let S stand for the solubility of BaF_2 in pure water at 25°C.

$$S(2S)^2 = K_{sp} = 1.7 \times 10^{-6} \text{ so that } S = 7.5 \times 10^{-3} = \left[Ba^{2+}\right]$$

The concentration of Ba^{2+} is then reduced to 1.0% of this by fluoride addition, or

$$[Ba^{2+}] = 7.5 \times 10^{-5} \text{ M and } \left[F^-\right] = \sqrt{K_{sp}/\left[Ba^{2+}\right]} = 0.15 \text{ M}$$

16.32 **a)** Assume that neither the Mg^{2+} ion nor the OH^- ion from the dissolution of the $Mg(OH)_2$ interacts further in the solution. Then, if S is the solubility of the $Mg(OH)_2$, the concentration of Mg^{2+} ion is S and the concentration of OH^- ion is $2S$. At equilibrium,

$$K_{sp} = 1.2 \times 10^{-11} = S\,(2S)^2 \text{ from which } S = 1.4 \times 10^{-4} \text{ mol L}^{-1}$$

b) If the solution is buffered at pH = 9, then the $[OH^-]$ is being held at 10^{-5} M. This concentration is *less* than what forms from the dissolution of the $Mg(OH)_2$ in pure water. After the dissolution of $Mg(OH)_2$ comes to equilibrium, the concentration of OH^- ion remains at 10^{-5} M because of the action of the buffer. Let S again represent the solubility of the salt. Then:

$$K_{sp} = 1.2 \times 10^{-11} = S\left(10^{-5}\right)^2$$

and the solubility is 0.12 mol L^{-1}.

16.34 **a)** Solubility will increase as CO_3^{2-} reacts with H_3O^+ to give HCO_3^-.
b) Solubility will show little change because HBr is a strong acid.
c) Solubility will increase as HS^- (from the dissolution of the MnS) reacts with H_3O^+ to give H_2S.

16.36 The tetrachlorothallate(III) complex ion forms by the reaction

$$Tl^3 + (aq) + 4\ Cl^-(aq) \rightleftharpoons TlCl_4^-(aq) \qquad \frac{\left[TlCl_4^-\right]}{\left[Tl^{3+}\right]\left[Cl^-\right]^4} = K_f = 1 \times 10^{18}$$

The large formation constant K_f means that the complex ion is heavily favored at equilibrium. Suppose that all of the $Tl^{3+}(aq)$ ion from dissolution of the $Tl(NO_3)_3$ reacts with the 0.50 mol of $Cl^-(aq)$ in solution to form the complex ion. The $Tl^{3+}(aq)$ is in excess, so the concentration of Cl^- would fall to zero, the concentration of $Tl^{3+}(aq)$ would be 0.025 mol L^{-1}, and the concentration of $TlCl_4^-(aq)$ would be 0.125 mol L^{-1}. Then imagine that equilibrium is attained by partial break-up of the complex. Because K_f is large, the equilibrium concentrations of $Tl^{3+}(aq)$ and $TlCl_4^-(aq)$ do not change significantly from the above values. No calculations are needed except to verify that the equilibrium concentration of Cl^- is indeed small (it equals 5×10^{-5} mol L^{-1}).

16.38 The two equilibria are

$$K^+(meth) + \text{crown}(meth) \rightleftharpoons \text{K-crown}^+(meth) \quad K = 1.14 \times 10^6$$
$$Cs^+(meth) + \text{crown}(meth) \rightleftharpoons \text{Cs-crown}^+(meth) \quad K = 2.75 \times 10^4$$

The equilibrium constants are fairly large, so both equilibria lie far to the right. The 18-crown-6 compound is in excess in the solution. Thus, effectively all of the K^+ and Cs^+ ion are consumed leaving 0.30 – 0.020 – 0.020 = 0.26 mol L^{-1} of crown and forming 0.020 mol L^{-1} of K-crown$^+$ and 0.020 mol L^{-1} of Cs-crown$^+$.

$$1.41 \times 10^6 = \frac{[\text{K-crown}^+]}{[K^+][\text{crown}]} = \frac{0.020}{[K^+]0.26} \text{ from which } [K+] = 5.5 \times 10^{-8} \text{ mol L}^{-1}$$

A similar computation on the Cs^+ equilibrium gives $[Cs^+] = 2.8 \times 10^{-6}$ mol L^{-1}.

16.40 The key equilibria are

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$
$$Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_f = 1.7 \times 10^7$$

Adding the second equation to the first gives

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \quad K = K_{sp}K_f = 2.7 \times 10^{-3}$$

Let x equal the equilibrium concentration of $Ag(NH_3)_2^+$. Then $[NH_3] = 1.0 - 2x$ and $[Cl^-] = x$. Substitute these values in the K expression and solve for x

$$2.7 \times 10^{-3} = \frac{x^2}{(1.0 - 2x)^2} \qquad \text{from which} \qquad x = 0.047$$

0.047 mol of AgCl(s) dissolves per liter. This is (0.047 mol)(143.3 g mol^{-1}) = 6.7 g.

16.42 The solution of $FeCl_3$ will be acidic. The Fe^{3+} ion interacts with water

$$Fe^{3+}(aq) + 2H_2O(l) \rightleftharpoons FeOH^{2+}(aq) + H_3O^+(aq)$$

The reaction can also be represented

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$

16.44 The reaction is

$$Fe(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5OH^+(aq) + H_3O^+(aq)$$

for which the K_a expression is

$$K_a = 3 \times 10^{-6} = \frac{[H_3O^+][Fe(H_2O)_5OH^+]}{[Fe(H_2O)_6^{2+}]}$$

The concentrations of $Fe(H_2O)_5OH^+$ and H_3O^+ are equal. Represent them by x. Then

$$3 \times 10^{-6} = \frac{x^2}{0.10 - x}$$

and $x = [H_3O^+] = 5.5 \times 10^{-4}$ mol L^{-1}. The pH is 3.3. This solution is less acidic that 0.1 M $Fe(NO_3)_3$, which has a pH of 1.6.

16.46 Treat the solution of $Ni(NO_3)_2$ containing a weak acid that donates one hydrogen ion. Neglect all other possible reactions. The equation is

$$Ni(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons Ni(H_2O)_5OH^+(aq) + H_3O^+(aq)$$

Assuming that the concentration of the $Ni(H_2O)_5OH^+$ ion equals that of the H_3O^+ ion, then both equal 1×10^{-5} M. Substituting in the K_a expression gives

$$K_a = \frac{(1 \times 10^{-5})^2}{(0.10 - 1 \times 10^{-5})} = 1 \times 10^{-9}$$

16.48 Assume that $Zn(OH)_2(s)$ is present at pH 14. Then

$$[Zn^{2+}][OH^-]^2 = K_{sp} = 4.5 \times 10^{-17}$$

$$[Zn^{2+}] = \frac{4.5 \times 10^{-17}}{(1.0)^2} = 4.5 \times 10^{-17} \text{ mol L}^{-1}$$

$$\frac{[Zn(OH)_4^{2-}]}{[Zn^{2+}][OH^-]^4} = K_f = 5 \times 10^{14}$$

$$[Zn(OH)_4^{2-}] = (5 \times 10^{14})(4.5 \times 10^{-17})(1.0)^4 = 2.2 \times 10^{-2} \text{ mol L}^{-1}$$

Now check the assumption

$$[Zn(OH)_4^{2-}] + [Zn^{2+}] = 2.2 \times 10^{-2} + 4.5 \times 10^{-17} = 0.022 \text{ mol L}^{-1} > 0.01 \text{ mol L}^{-1}$$

The assumption was false. In fact $Zn(OH)_2(s)$ is *not* present at equilibrium. Recalculate the concentrations using

$$\frac{[Zn^{2+}]}{[Zn(OH)_4^{2-}]} = \frac{1}{K_f[OH^-]^4} = \frac{1}{5 \times 10^{14}[1]^4} = 2 \times 10^{-15}$$

$$[Zn(OH)_4^{2-}] = 0.010 \text{ mol L}^{-1} \text{ and } [Zn^{2+}] = 2 \times 10^{-17} \text{ mol L}^{-1}$$

In the second case (at pH 13) again assume that $Zn(OH)_2(s)$ is present at equilibrium

$$\left[Zn^{2+}\right] = \frac{\left(4.5\times10^{-17}\right)}{\left(0.10\right)^2} = 4.5\times10^{-15}\text{mol L}^{-1}$$

$$\left[Zn\left(OH\right)_4^{2-}\right] = \left(5\times10^{14}\right)\left(4.5\times10^{-15}\right)\left(0.1\right)^4 = 2.2\times10^{-4}\text{mol L}^{-1}$$

Checking the assumption in this case gives

$$\left[Zn\left(OH\right)_4^{2-}\right] + \left[Zn^{2+}\right] = 2.2\times10^{-4} < 0.10 \text{ mol L}^{-1}$$

The assumption was correct: a precipitate forms.

16.50 **a)** If the F^- ion concentration exceeds 8.8×10^{-6} M, then CaF_2 precipitates. If it exceeds 4.1×10^{-3} M, then BaF_2 precipitates. These two concentrations are calculated by substitution into the two K_{sp} expressions. Keeping $[F^-]$ below 4.1×10^{-3} M allows only CaF_2 to precipitate.
b) If the $[F^-]$ is held at 4.1×10^{-3} mol L^{-1}, then the concentration of Ca^{2+} in equilibrium with it and the $CaF_2(s)$ is only 2.3×10^{-6} mol L^{-1}. This amounts to 4.6×10^{-6} of the 0.50 mol L^{-1} originally present.

16.52 The $BaSO_4$ is more insoluble than the $CaSO_4$. Substitution of the given $[Ca^{2+}]$ concentration into the K_{sp} expression for $CaSO_4$ gives the concentration of SO_4^{2-} at which $CaSO_4$ just starts to precipitate. It is 3.0×10^{-4} mol L^{-1}. At this concentration of sulfate ion, $[Ba^{2+}]$ is 3.7×10^{-7} mol L^{-1}, according to the K_{sp} expression for $BaSO_4(s)$.

16.54 From text Table 16.3,

$$CdS\left(s\right) + H_2O\left(l\right) \rightleftharpoons Cd^{2+}\left(aq\right) + OH^-\left(aq\right) + HS^-\left(aq\right) \quad K = 7\times10^{-28}$$

Add to this equilibria

$$HS^-\left(aq\right) + H_3O+\left(aq\right) \rightleftharpoons H_2S\left(aq\right) + H_2O\left(l\right) \quad K = \frac{1}{K_a}$$

$$H_3O+\left(aq\right) + OH^-\left(aq\right) \rightleftharpoons 2\ H_2O\left(l\right) \quad K = \frac{1}{K_W}$$

This gives

$$CdS\left(s\right) + 2\ H_2O+\left(aq\right) \rightleftharpoons Cd^{2+}\left(aq\right) + H_2S\left(aq\right) + 2\ H_2O\left(l\right)$$

$$\text{for which } \frac{\left[Cd^{2+}\right]\left[H_2S\right]}{\left[H_3O^+\right]^2} = \frac{K}{K_a K_w} = \frac{7\times10^{-28}}{(9.1\times10^{-8})(1.0\times10^{-4})} = 7.7\times10^{-7}$$

Interesting $\left[H_2S\right] = 0.10$ M and $\left[H_3O^+\right] = 1.0\times10^{-3}$M and solving for $\left[Cd^{2+}\right]$gives

$$\left[Cd^{2+}\right] = 8\times10^{-12}\ \text{M}$$

16.56 Follow the procedure in problem **16.40.** The condition for Mn^{2+} to remain in solution is

$$\frac{\left[Mn^{2+}\right]\left[H_2S\right]}{\left[H_3O^+\right]^2} < \frac{K}{K_a K_w} = \frac{3\times10^{-14}}{\left(9.1\times10^{-8}\right)\left(1.0\times10^{-14}\right)} = 3.3\times10^7$$

Inserting $[Mn^{2+}] = 0.050$ M and $[H_2S] = 0.10$ M gives

$$[H_3O^+]^2 > \frac{[Mn^{2+}][H_2S]}{3.3\times10^7} = \frac{(0.050)(0.10)}{3.3\times10^7} = 1.5\times10^{-10}$$

$$\left[H_3O^+\right] > 1.2\times10^{-5};\quad pH < 4.9$$

Now use the expression for CdS(s) dissolution from problem **16.40**:

$$\left[Cd^{2+}\right] = \frac{\left[H_3O^+\right]^2}{\left[H_2S\right]}\left(7.7\times10^{-7}\right) = \frac{\left(1.2\times10^{-5}\right)^2}{0.10}\left(7.7\times10^{-7}\right) = 1\times10^{-15}\ \text{M}$$

16.58 The chemical equation is

$$MgNH_4PO_4\cdot 6H_2O(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + 6H_2O(l)$$

The six moles of water of crystallization are included in the equation to maintain a formal balance. They join the rest of the water in the solution, however, and are not included in the following K_{sp} expression:

$$\left[Mg^{2+}\right]\left[NH_4^+\right]\left[PO_4^{3-}\right] = K_{sp} = 2.3\times10^{-13}$$

Once this compound is dissolved, because $PO_4^{3-}(aq)$ is a stronger base than NH_3, the reaction $NH_4^+(aq) + PO_4^{3-}(aq) \rightleftharpoons NH_3(aq) + HPO_4^{2-}(aq)$ will occur.

16.60 The dissolution reaction is represented

$$AgClO_4(s) \rightleftharpoons Ag^+(aq) + ClO_4^-(aq)$$

The large concentration of ClO_4^- present in 60 percent perchloric acid solution reduces the solubility of the $AgClO_4$ (the common-ion effect).

16.62 Use the solubility-product expression

$$\left[Ca^{2+}\right]\left[F^-\right]^2 = K_{sp} = 3.9\times10^{-11}$$

With $\left[Ca^{2+}\right] = 0.0020$ M, the largest $\left[F^-\right]$ that can be tolerated before CaF_2 tends to precipitate is 14×10^{-5} M. This exceeds the recommended $F^-(aq)$ concentration.

16.64 Use the letter C to refer to $CaCO_3$ and B to refer to $BaCO_3$. For $CaCO_3$:

$$S_C = 7\times10^{-3}\,\text{g L}^{-1}\times\frac{1\text{ mol}}{100\text{ g}} = 7\times10^{-5}\ \text{mol L}^{-1}\ \text{ so that }\ K_{sp,C} = S_C^2 = 5\times10^{-9}$$

Write the K_{sp} expressions for dissolution of the two carbonates and divide one by the other:

$$\frac{\left[Ba^{2+}\right]\left[CO_3^{2-}\right]}{\left[Ca^{2+}\right]\left[CO_3^{2-}\right]} = \frac{K_{sp,B}}{K_{sp,C}}$$

Just after the precipitation of $CaCO_3$ has begun, both dissolution reactions are at equilibrium, and the concentration of Ba^{24+} has been reduced to 0.10 of what it was originally. Therefore

$$\frac{(0.10)\left[Ca^{2+}\right]}{\left[Ca^{2+}\right]}=\frac{K_{sp,B}}{K_{sp,C}}$$

$$K_{sp,B}=(0.10)K_{sp,C}=0.10\left(5\times10^{-9}\right)=5\times10^{-10}$$

16.66 **a)** If all but 0.1 percent of the Fe^{3+} ion has been precipitated, then

$$\left[Fe^{3+}\right]=0.001\left(0.01\text{ mol L}^{-1}\right)=1\times10^{-5}\text{ mol L}^{-1}$$

Since the solution is saturated with $Fe(OH)_3$,

$$\left[OH^-\right]^3=\frac{10^{-36}}{1\times10^{-5}}=10^{-31}\Rightarrow\left[H_3O^+\right]=\frac{1\times10^{-14}}{\sqrt[3]{10^{-31}}}=2\times10^{-4}\text{ mol L}^{-1}$$

for a pH of 3.7. At a higher pH, an even smaller fraction of the Fe^{3+} ion remains in solution.

b) $Ni(OH)_2$ tends to precipitate when

$$Q=\left[Ni^{2+}\right]\left[OH^-\right]^2\geq K_{sp}=6\times10^{-18}$$

If $[Ni^{2+}]$ = 0.01 mol L^{-1}, then $[OH^-]^2 < 6\times10^{-16}$ to avoid precipitation of $Ni(OH)_2$, or $[OH^-] < 2.4\times10^{-8}$ mol L^{-1}. This corresponds to $[H_3O^+] > 4\times10^{-7}$ mol L^{-1}, or pH < 6.4.

Between pH 3.7 and 6.4, Fe^{3+} and Ni^{2+} could, in principle, be separated effectively by precipitation of $Fe(OH)_3$.

16.68 Two dissolution-precipitation equilibria take place simultaneously. They are

$$BaSO_4(s)\rightleftharpoons Ba^{2+}(aq)+SO_4^{2-}(aq)\ \text{ and }\ AgCl(s)\rightleftharpoons Ag^+(aq)+Cl^-(aq)$$

Solutions of Ag_2SO_4 and $BaCl_2$ are mixed. Both substances are dissociated into ions in aqueous solution. The concentrations of the four ions after the mixing, but before any precipitation has occurred are $[Ba^{2+}]$ = 0.020 M, [Ag+] = 0.020 M, $[Cl^-]$ = 0.040 M, and $\left[SO_4^{2-}\right]=0.010$ M. Assume that the Ba^{2+} and the SO_4^{2-} react completely to form $BaSO_4(s)$. Then the concentration of the sulfate is zero, and the concentration of the barium ion, which is in excess in the precipitation reaction, is 0.010 M. Substituting this 0.010 M into the K_{sp} expression gives $\left[SO_4^{2-}\right]=1.1\times10^{-8}$ M, which is indeed very close to zero. In the same way, Cl^- is in excess relative to Ag^+. At equilibrium, its concentration will be 0.020 M. The K_{sp} for AgCl then gives $\left[Ag^+\right]=8.0\times10^{-9}$ M.

16.70 When CaO dissolves in water, the oxide ion reacts immediately with water to furnish hydroxide ions. The chemical equation is

$$CaO(s)+H_2O(l)\rightleftharpoons Ca^{2+}(aq)+2\ OH^-(aq)$$

for which the equilibrium constant expression is $K=[Ca^{2+}][OH^-]^2$.
The dissolution of CaO(*s*) in acid is better represented as

$$CaO(s) + 2H_3O^+(aq) \rightleftharpoons Ca^{2+}(aq) + 3H_2O(l)$$

The equilibrium constant is then

$$\frac{[Ca^{2+}]}{[H_3O^+]^2} = \frac{K}{K_w^2}$$

16.72 A chemical reaction occurs at each of the three steps in the process

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

$$AgCl(s) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

$$Ag(NH_3)_2^+(aq) + 2H_3O^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + 2NH_4^+(aq) + 2\ H_2O(l)$$

16.74 **a)** Suppose that x mol L^{-1} of CaC_2O_4 dissolves at equilibrium. Then $[Ca^{2+}] = x$. The $C_2O_4^{2-}$ ion from the dissolution can react with $H_2C_2O_4$ according to

$$C_2O_4^{2-}(aq) + H_2C_2O_4(aq) \rightleftharpoons 2\ HC_2O_4^-(aq) \qquad \frac{[HC_2O_4^-]^2}{[C_2O_4^{2-}][H_2C_2O_4]} = \frac{K_{a1}}{K_{a2}} = 920$$

Imagine that this reaction proceeds until at equilibrium $[C_2O_4^{2-}] = y$. Then $(x - y)$ mol L^{-1} of oxalate has reacted, and

$$[HC_2O_4^-] = 2(x-y) \text{ and } [H_2C_2O_4] = 1.0 - (x-y)$$

Insert the equilibrium concentrations in terms of x and y into the K_a and K_{sp} expressions

$$\frac{(2(x-y))^2}{y(1-x+y)} = \frac{4(x-y)^2}{y(1-x+y)} = 920 \qquad \text{and} \qquad [Ca^{2+}][C_2O_4^{2-}] = K_{sp} = xy = 2.6 \times 10^{-9}$$

Now solve the K_{sp} expression for y obtaining $y = 2.6 \times 10^{-9}/x$. Substitute this result for y into the denominator of the K_a expression:

$$\frac{4(x-y)^2 x}{(2.6 \times 10^{-9})(1-x+y)} = 920 \qquad \text{which gives} \qquad \frac{x(x-y)^2}{1-x+y} = 5.98 \times 10^{-7}$$

Assume that $y << x$. Then $x^3/(1-x) = 5.98 \times 10^{-7}$. Now assume that $x << 1$. Then $x^3 = 5.98 \times 10^{-7}$ and $x = 8.4 \times 10^{-3}$. This is in fact much less than 1. Next, obtain y

$$y = \frac{2.6 \times 10^{-9}}{8.4 \times 10^{-3}} = 3.1 \times 10^{-7}$$

which is clearly much less than x: the first simplifying assumption is also justified. The solubility of the calcium oxalate equals x or $[Ca^{2+}] = 8.4 \times 10^{-3}$ mol L^{-1}.

b) At equilibrium $\left[Ca^{2+}\right] = \left[C_2O_4^{2-}\right]$ (this assumes that neither ion reacts with H_2O or any other species in solution). The K_{sp} expression gives $[Ca^{2+}]^2 = 2.6 \times 10^{-9}$ from which $[Ca^{2+}] = 5.1 \times 10^{-5}$ mol L^{-1}. This result is the solubility.

c) The $C_2O_4^{2-}$ ion decreases its concentration by reacting with $H_2C_2O_4$. By LeChâtelier's principle, the system responds by more extensive dissolution of CaC_2O_4.

16.76 Mixing the solutions as described amounts to making a solution that is initially 0.100 M in $(HgCl^+)NO_3$. Following the hint, construct a correspondence between the species taking part in the complexation equilibria in this solution and the species taking part in the amphoteric equilibria that exist in a solution that is initially 0.100 M in $NaHCO_3$ (Section 15.8). Let the correspondence also include the equilibrium constants:

Complex		Acid-Base
$HgCl_2$	equivalent to	H_2CO_3
$HgCl^+$	equivalent to	HCO_3^-
Hg^{2+}	equivalent to	CO_3^{2-}
Cl^-	equivalent to	H_3O^+
NO_3^-	equivalent to	Na^+
$1/K_2$	equivalent to	K_{a1}
$1/K_1$	equivalent to	K_{a2}
0	equivalent to	K_w

In the acid-base equilbria, the focus is on dissociation; in the complexation case the focus on formation. The use of the reciprocals of the formation constants K_1 (for the formation of $HgCl^+$ from Hg^{2+}) and K_2 (for the formation of $HgCl_2$ from $HgCl^+$) in the preceding table permits a near-perfect analogy to the amphoteric case. Nothing in the complexation case corresponds to the hydroxide ion. This is why the analog of K_w to zero. Translating according to the preceding table into the equation for $[H_3O^+]$ in text Section 15.8 gives

$$\left[Cl^-\right]^2 = \frac{\left[HgCl^+\right]_0 / K_1 K_2}{1/K_2 + \left[HgCl^+\right]}$$

Assume that $1/K_2 << \left[HgCl^+\right]_0$ (to be checked later) and neglect it in the denominator. Then

$$\left[Cl^-\right] = \sqrt{\frac{1}{K_1 K_2}} = \sqrt{\frac{1}{\left(5.5 \times 10^6\right)\left(3 \times 10^6\right)}} = 2.46 \times 10^{-7} \text{ mol L}^{-1}$$

Write

$$\frac{[HgCl_2]}{[HgCl^+][Cl^-]} = K_2 \text{ from which } [HgCl_2] = K_2[Cl^-][HgCl^+] = 0.739[HgCl^+]$$

and

$$\frac{[HgCl^+]}{[Hg^{2+}][Cl^-]} = K_1 \text{ from which } [Hg^{2+}] = \frac{1}{K_1[Cl^-]}[HgCl^+] = 0.739[HgCl^+]$$

The fact that $[Hg^{2+}] = [HgCl_2]$ results from stoichiometry as well. Adding total concentrations of Hg-containing species gives

$$0.100 = [HgCl^+] + 2(0.739)[HgCl^+] \qquad \text{from which} \qquad [HgCl^+] = 0.040 \text{ mol L}^{-1}$$

This confirms that $[HgCl^+]$ is in fact very much larger than $1/K_2$. Finally

$$[Hg^{2+}] = [HgCl_2] = 0.739[HgCl^+] = 0.030 \text{ mol L}^{-1}$$

16.78 $Pt(OH)_6^{2-}(aq) + H_2O(l) \rightarrow Pt(H_2O)(OH)_5^-(aq) + OH^-(aq)$

16.80 By LeChâtelier's principle, increased pressure favors the state with smaller volume, namely the separated water and salt. The solubility of this salt will decrease as the pressure is increased.

16.82 **a)** The chemical amount of CO_2 is

$$n_{CO_2} = \frac{PV}{RT} = \frac{(0.972 \text{ atm})(0.20 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(373 \text{ K})} = 6.35 \times 10^{-3} \text{ mol}$$

This must have resulted from the same amount of dissolved carbonate in the solution. Thus the concentrations of carbonate and strontium ions were

$$[CO_3^{2-}] = [Sr^{2+}] = \frac{6.35 \times 10^{-3} \text{ mol}}{1.44 \text{ L}} = 4.41 \times 10^{-3} \text{ mol L}^{-1}$$

The molar solubility is 4.4×10^{-3} mol L^{-1}.

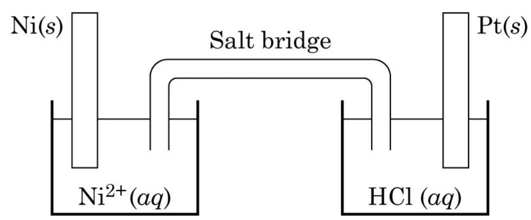
b) $K_{sp} = [Sr^{2+}][CO_3^{2-}] = (4.41 \times 10^{-3})^2 = 1.9 \times 10^{-5}$

c) Strontium and carbonate ions may react with water to form other ionic species. This will change the relationship between the K_{sp} and the solubility.

Chapter 17

Electrochemistry

17.2 When the two electrodes in the following diagram are connected by a wire, electrons flow from the left electrode as metallic nickel is oxidized to Ni^{2+} at the left-hand electrode; the electrons are taken up by H^+ ions at the right-hand electrode. In the salt bridge, negative ions flow from right to left and positive ions from left to right.



Bubbles of gaseous hydrogen are released to rise through the solution in the right-hand cell compartment. The overall reaction is

$$Ni(s) + 2HCl(aq) \rightarrow H_2(g) + NiCl_2(aq)$$

17.4 The quantity of electricity is 0.9600 mol of electrons, as shown by dividing the number of coulombs by the Faraday constant. Dissolving 1 mol of Ni to give $Ni^{2+}(aq)$ requires passage of 2 mol of electrons, so the maximum amount of Ni dissolved is 0.4800 mol.

17.6 **a)** The balanced equation is $Zn(s) + Cd^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cd(s)$.

b) The product of the (steady) current in amperes and the time in seconds is the charge in coulombs. It is 1.36×10^4 C. Dividing by the Faraday constant gives the chemical amount of electrons, 0.141 mol.
c) Every 1 mol of electrons that passes through the cell oxidizes 1/2 mol of zinc. Hence 0.0703 mol of zinc is oxidized. This is 4.60 g of zinc and is the mass lost by the zinc electrode.
d) Every 1 mol of electrons that passes through the cell reduces 1/2 mol of cadmium(II) ions. This is 0.0703 mol of Cd^{2+}, or 7.91 g of Cd^{2+}. This is the mass gained by the cadmium electrode.

17.8 Multiplying the relative mass of hydrogen liberated by 1 gives close to the known atomic weight of H. Similarly multiplying the given relative mass by 2 for oxygen, by 1 for chlorine and by 2 for tin gives close to the respective relative atomic masses of the elements. The absolute values of the oxidation states of the four elements (hydrogen, oxygen, chlorine, and tin) are therefore in the ratio 1 to 2 to 1 to 2. This follows from Faraday's law that a given amount of charge liberates different substances in proportion to their molar masses (atomic masses) divided by the absolute values of their oxidation numbers.

The hydrogen is liberated at the cathode and must come from the reduction of +1 hydrogen (H^+); other positive oxidation states of hydrogen are nearly unknown. The gaseous oxygen is liberated at the *anode*. The species that formed the gas therefore *lost* electrons to do so; the oxidation state of the oxygen is -2 . The oxidation state for chlorine is -1 . The oxidation state for tin is +2.

17.10 a) Anode: $C(s) + 2\ O^{2-}(cryo) \rightarrow CO_2(g) + 4\ e^-$ Cathode: $Al^{3+}(cryo) + 3e^- \rightarrow Al(l)$
Overall: $3\ C(s) + 6\ O^{2-}(cryo) + 4\ Al^{3+}(cryo) \rightarrow 3\ CO_2(g) + 4\ Al(l)$

b) $m_{Al} = 24\ h\left(\frac{3600\ s}{1\ h}\right)\left(\frac{50\ kC}{1\ s}\right)\left(\frac{1\ mol\ e^-}{96485\ C}\right)\left(\frac{1\ mol\ Al}{3\ mol\ e^-}\right)\left(\frac{26.98\ g\ Al}{1\ mol\ Al}\right) = 403\ kg\ Al$

17.12 Use the equation:

$$\Delta G = -n\mathcal{F}\Delta\mathcal{E} = w_{elec,max}$$

The $\Delta\mathcal{E}$ is 0.48 V, and $\mathcal{F}$ is 96,485 C mol^{-1}. If 1 mol of zinc were oxidized, then n would equal 2 mol, and $w_{elec,max}$ would be -92.6 kJ . But 1 g of zinc is much less than 1 mol of zinc; it is only 0.0153 mol. Therefore $n = 2 \times 0.0153$ mol in the formula, and the maximum work done *on* the cell is -1.4 kJ . The maximum work done by the cell is the negative of this, or +1.4 kJ per gram of zinc consumed.

17.14 a) The reduction of Fe^{3+} to Fe^{2+} has $\mathcal{E}° = 0.770$ V, and the reduction of Cd^{2+} to Cd has $\mathcal{E}° = -0.4026$ V . In this galvanic cell with all species in their standard states, the half-reaction $Fe^{3+} + e^- \rightarrow Fe^{2+}$ takes place at the cathode, and the oxidation $Cd \rightarrow Cd^{2+} + 2\ e^-$ takes place at the anode. Only in this way is $\Delta\mathcal{E}°$ of the cell positive.

b) $\Delta\mathcal{E}° = \mathcal{E}°(\text{cathode}) - \mathcal{E}°(\text{anode}) = 0.770 - (-0.4026) = 1.173$ V.

17.16 a) The increase in the concentration of Cl^- ion means that $Cl_2(g)$ is reduced as the cell operates spontaneously. The half-reaction at the cathode, where reduction occurs, is accordingly $Cl_2 + 2e^- \rightarrow 2\ Cl^-$. At the anode, the half-reaction is $Ga \rightarrow Ga^{3+} + 3\ e^-$.

b) The overall voltage is $\Delta\mathcal{E}°$ and equals 1.918 V. It also equals the standard reduction potential of the reduction half-reaction minus the standard reduction potential of the oxidation half-reaction The reduction is the conversion of Cl_2 to Cl^-, which has $\mathcal{E}°$ equal to 1.3583 V (Appendix E). Hence:

$$\Delta\mathcal{E}° = 1.918 = \mathcal{E}°\ (\text{cathode}) - \mathcal{E}°\ (\text{annode}) = 1.3583 - x$$

It follows that x, the reduction potential for the Ga^{3+}/Ga half-cell, is -0.560 V.

17.18 An acidic solution of potassium perchlorate would be an oxidizing agent.

17.20 The standard reduction potentials for ClO_3^-, ClO^-, and Cl_2 in acidic aqueous media are 1.47, 1.63, and 1.3583 V respectively, according to text Appendix E. This means that at a given concentration at pH 0, a solution of NaClO is the strongest bleach, despite the fact that the change in oxidation number it experiences is small. At pH 0, the ClO^- ion, a fairly strong base, picks up a hydrogen ion. so the species in the half-equation is HClO. At pH 0 the reduction potential of O_3 to O_2 is 2.07 V (this value does not appear in text Appendix E). Therefore ozone is a stronger bleach than any of the chlorine bleaches.

17.22 **a)** H_2O_2 is the strongest oxidizing agent because it is the most easily reduced in this group; it appears near the top left in Appendix E.
b) Sc is the strongest reducing agent because it is the most easily oxidized in this group; it appears more toward the bottom right in Appendix E.
c) Look for a substance on the left side of an arrow in Appendix E and in a row between Fe and Cu. The answer is Sn^{2+}.

17.24 **a)** The desired half-reaction (label it 3) is half-reaction 2 given in the problem minus half-reaction 1. All three $\mathcal{E}°$'s must be weighted by the number of electrons transferred:

$$\mathcal{E}_3^\circ = \frac{n_2\mathcal{E}_2^\circ - n_1\mathcal{E}_1^\circ}{n_3} = \frac{(2)(1.25\text{ V}) - (1)(-0.37\text{ V})}{1} = 2.87\text{ V}$$

b) This reaction equals half-reaction 3 in part **a)** minus half-reaction 1. $\Delta\mathcal{E}^\circ = 2.87 - (-0.37) = 3.24\text{ V}$. The standard potential exceeds zero, so, yes, $Tl^{2+}(aq)$ will tend to disproportionate when in its standard state.

17.26 **a)** ClO^- tends to disproportionate spontaneously at pH 14 to give Cl^- and ClO_2^-. The $\Delta\mathcal{E}^\circ$ of the reaction is 0.90 – 0.59 = 0.31 V.

b) According to the reduction potentials given in the problem ClO^- is oxidized to ClO_2^- more readily than Cl^- is oxidized to ClO^- at pH 14; the ClO^- is the stronger reducing agent under these conditions. However, neither of these is a very good reducing agent.

17.28 Calculate the standard potential difference of the cell from the data in Appendix E. At the anode is the $Ag|Ag^+$ couple; at the cathode is the $Cl_2|Cl^-$ couple. For the overall cell reaction $2\text{ Ag}(s) + Cl_2(g) \rightarrow 2Ag^+(aq) + 2\text{ Cl}^-(aq)$, the $\Delta\mathcal{E}^\circ$ is 1.3583 – 0.7996 = 0.5587 V. This standard potential difference must be corrected for the non-standard concentrations in this cell. At 25°C:

$$\Delta\mathcal{E} = \Delta\mathcal{E}^\circ - \frac{0.0592\text{ V}}{n}\log\, Q = 0.5587\text{ V} - \frac{0.0592\text{ V}}{2}\log\left(\frac{[Ag^+]^2[Cl^-]^2}{P_{Cl_2}}\right)$$

$$\Delta\mathcal{E} = 0.5587\text{ V} - \frac{0.0592\text{ V}}{2}\log\left(\frac{(0.25)^2(0.016)^2}{1.00}\right) = 0.701\text{ V}$$

17.30 Figure the half-cell potential at 25°C using the Nernst equation and the standard reduction potential from Appendix E. The half-reaction is $I_2(s) + 2\,e^- \rightarrow 2\text{ I}^-(aq)$ for which $\mathcal{E}^\circ$ is 0.535 V. Then:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0592\text{ V}}{n_{hc}}\log[I^-]^2 = 0.535\text{ V} - \frac{0.0592\text{ V}}{2}\log[1.5\times10^{-6}]^2 = 0.880\text{ V}$$

17.32 Write the Nernst equation for the redox reaction

$$Cu(s) + Br_2(l) \rightarrow Cu^{2+}(aq) + 2\text{ Br}^-(aq)$$

at 25°C and use it to calculate the unknown concentration. The standard potential difference of the cell is figured from the standards potentials in Appendix E. It is

$$\Delta\mathcal{E}^\circ = \mathcal{E}\text{ (cathode)} - \mathcal{E}\text{ (anode)} = 1.065 - 0.3402 = 0.725\text{ V}$$

The Nernst equation is then:

$$\Delta\mathcal{E} = 0.963 \text{ V} = 0.725 \text{ V} - \frac{0.0592 \text{ V}}{2}\log\left(\left[Cu^{2+}\right]\left[Br^-\right]^2\right)$$

Inserting $\left[Cu^{2+}\right] = 1.00$ M and solving for [Br⁻] gives $\left[Br^-\right] = 10^{-4.02} = 9.5 \times 10^{-5}$ M.

17.34 **a)** Write half-equations for the reduction (at the cathode) and oxidation (at the anode)

$$Cr_2O_7^{2-}(aq) + 14\ H_3O^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 21\ H_2O(l) \quad \text{cathode}$$
$$6\ I^-(aq) \rightarrow 3\ I_2(s) + 6e^- \quad \text{anode}$$

Find the standard reduction potentials for these couples in Appendix E and combine them to obtain the standard potential of the cell:

$$\Delta\mathcal{E}^\circ = \mathcal{E}^\circ(\text{cathode}) - \mathcal{E}^\circ(\text{anode}) = 1.33 - 0.535 = 0.80 \text{ V}$$

b) At 25°C for this cell

$$\Delta\mathcal{E} = \Delta\mathcal{E}^\circ - \frac{0.0592 \text{ V}}{n}\log Q = \frac{0.0592 \text{ V}}{6}\log\left(\frac{\left[Cr^{3+}\right]^2}{\left[Cr_2O_7^{2-}\right]\left[I^-\right]^6\left[H_3O^+\right]^{14}}\right)$$

Insert the known voltages and concentrations

$$0.87 \text{ V} = 0.795 \text{ V} - \frac{0.0592 \text{ V}}{6}\log\left(\frac{\left[Cr^{3+}\right]^2}{(1.5)(0.40)^6(1.0)^{14}}\right)$$

Solving gives $\left[Cr^{3+}\right] = 10^{-5}$M.

17.36 The standard potential difference of the reaction is the standard reduction potential for the conversion of mercury(II) to mercury(I) minus the standard reduction potential for the conversion of gold(III) to gold(0): $\Delta\mathcal{E}^\circ = 0.905 - 1.42 = -0.515$ V. The quantity n in the reaction as given in the problem is 6, so at 25°C:

$$\log K = \frac{n}{0.0592 \text{ V}}\Delta\mathcal{E}^\circ = \frac{6}{0.0592 \text{ V}}(-0.515 \text{ V}) = -52.2$$

The equilibrium constant at 25°C for the reaction as written in the problem is $K_{298} = 10^{-52}$. The second question really concerns the reverse of the reaction written in the problem. The equilibrium constant of the reverse reaction is the reciprocal of the K just computed:

$$\frac{1}{6 \times 10^{-53}} = \frac{\left[Hg^{2+}\right]^6}{\left[Au^{3+}\right]^2\left[Hg_2^{2+}\right]^3}$$

After the Hg_2^{2+} and Au^{3+} are mixed, but before the reaction starts, their concentrations are both 0.500 M. The equilibrium constant is very large, so the reaction proceeds until the Hg_2^{2+} ion, which is the limiting reactant, is essentially all consumed. Suppose that *all* of the 0.500 M Hg_2^{2+} reacts. The concentration of Hg^{2+} formed is then 1.00 M, and the concentration of excess Au^{3+} is 0.167 M, by the stoichiometry of the reaction. Let the concentration of Hg_2^{2+} actually left at equilibrium equal x. Then $\left[Au^{3+}\right] = 0.167 + 2/3x$ M, and $\left[Hg^{2+}\right] = 1.00 - 2x$ M at equilibrium. Substitute these expressions into the equilibrium law:

$$\frac{1}{6 \times 10^{-53}} = \frac{(1.00 - 2x)^6}{(0.167 + 2/3x)^2 (x)^3}$$

Because x is certainly very small compared to 0.167, this equation becomes

$$\frac{1}{6 \times 10^{-53}} \approx \frac{(1.00)^6}{(0.167)^2 (x)^3}$$

Solving gives $x = 10^{-17}$ M. This is the equilibrium concentration of Hg_2^{2+} ion. The equilibrium concentration of Au^{3+} ion is 0.167 M, and the equilibrium concentration of Hg^{2+} ion is 1.00 M.

17.38 The reaction in the problem is the second of the following half-reactions subtracted from the first

$$Hg^{2+}(aq) + e^- \rightarrow \tfrac{1}{2}Hg_2^{2+}(aq) \qquad \tfrac{1}{2}Hg_2^{2+}(aq) + e^- \rightarrow Hg(l)$$

The $\Delta\mathcal{E}^0$ for the reaction is accordingly the $\mathcal{E}^0$ for the second half-reaction subtracted from the $\mathcal{E}^0$ for the first. Taking values from Appendix E, $\Delta\mathcal{E}^0 = 0.905 - 0.7961 = 0.109$ V. Although the half-equations in Appendix E are written with coefficients that are twice the coefficients in the above, the standard potential difference is the same; it does not depend on the amount of substance that reacts. Inserting this number into the relationship (at 25°C) between the equilibrium constant and the standard potential difference gives:

$$\log_{10} K_{298} = \frac{n}{0.0592}\Delta\mathcal{E}^0 = \frac{1}{0.0592 \text{ V}}(0.109 \text{ V}) = 1.84 \qquad \text{so that} \qquad K_{298} = 69$$

17.40 Figure the standard potential difference for the reaction

$$\Delta\mathcal{E}^0 = \mathcal{E}^0\left(Ag^+|Ag\right) - \mathcal{E}^0\left(H_3O^+|H_2\right) = 0.7996 - (0) = 0.7996 \text{ V}$$

Write the Nernst equation at 25° C

$$\Delta\mathcal{E} = \Delta\mathcal{E}^0 - \frac{0.0592}{n}\log\frac{\left[H_3O^+\right]}{\left[Ag^+\right]P_{H_2}^{1/2}}$$

and substitute all of the known values

$$1.030 = 0.7996 - \frac{0.0592}{1}\log\frac{\left[H_3O^+\right]}{(1.00)(1.00)}$$

From this equation, $\left[H_3O^+\right]$ is 1.28×10^{-4}M. The pH in the buffer solution in the cell is 3.89. Now, compute the K_a of the benzoic acid by substitution in the acid ionization equilibrium expression

$$K_a = \frac{\left[H_3O^+\right]\left[C_6H_5COO^-\right]}{\left[C_6H_5CHOOH\right]} = \frac{(1.28 \times 10^{-4})(0.050)}{(0.10)} = 6.4 \times 10^{-5}$$

17.42 a) Pb(*s*) is oxidized; H_3O^+ is reduced.

$$\Delta\mathcal{E}^0 = \mathcal{E}^0\left(H_3O^+\middle|H_2\right) - \mathcal{E}^0\left(Pb^{2+}\middle|Pb\right) = 0 - (-0.1263) = 0.1263 \text{ V}$$

b) At 25°C for this cell and the quantities specified in the problem

$$\Delta\mathcal{E} = \Delta\mathcal{E}^0 - \frac{0.0592}{n}\log\frac{\left[Pb^{2+}\right]P_{H_2}}{\left[H_3O^+\right]^2} \text{ which gives } 0.22 = 0.1263 - \frac{0.0592}{2}\log\frac{\left[Pb^{2+}\right]1.0}{\left[1.00\right]^2}$$

Solving gives $\left[Pb^{2+}\right] = 7\times10^{-4}$ mol L^{-1} $\approx 10^{-3}$ mol L^{-1}.

c) Presumably the lead concentration in part **b)** is in equilibrium with the 0.15 M Cl^- ion. Use the K_{sp} expression: $K_{sp} = \left[Pb^{2+}\right]\left[Cl^-\right]^2 = \left(6.8\times10^{-4}\right)\left(0.15\right)^2 = 2\times10^{-5}$.

17.44 Ferrocene methanol is a reversible redox couple so the CV looks very much like that in Example 17.10, with the midpoint between the reduction and oxidation waves located at +0.64 V. The ferrocene cation Fc^+ is reduced to ferrocene at potentials more negative than +0.64 V and ferrocene is oxidized to Fc^+ at potentials more positive than +0.64 V.

17.46

$$E = \frac{hc}{\lambda} = \frac{(4.135\times10^{-15}eV\cdot s)(3\times10^{8}m\cdot s^{-1})}{(520\times10^{-9}m)} = 2.4eV$$

Thus the redox potential associated with the LUMO must be:

$$E_{LUMO} = \frac{(2.4-0.5)eV}{-e} = -1.9V$$

17.48 $E_{HOMO} = E_{LUMO} + 2.3V = 1.0V$ which is not sufficiently positive to oxidize water (1.229V).

17.50 The conduction band of $SrTiO_3$ lies at -0.7 V and the valence band at + 2.5 V, under the same conditions as those used for the sensitized TiO_2 electrode in the *Connection to Energy*. The LUMO of the sensitizer should lie at potentials more negative than -0.7 V for electron injection into the strontium titanate conduction band and the HOMO of the sensitizer should lie at potentials more positive than 0.35 V, the reduction potential of the I/I_3^- couple.

17.52 The overall reaction is

$$Zn(s) + HgO(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Hg(l)$$

for which

$$\Delta G^0_{298} = 1(-553.5) + 1(0) - 1(0) - 1(-58.56) - 1(-237.18) = -257.76 \text{ kJ}$$

Compute the $\Delta\mathcal{E}^0_{298}$ by substitution

$$\Delta\mathcal{E}^0 = -\frac{\Delta G^0_{298}}{n\mathcal{F}} = -\frac{-257.76\times10^3 \text{ J}}{(2 \text{ mol})(96485 \text{ C mol}^{-1})} = 1.336 \text{ V}$$

17.54 **a)** The cell reaction is

$$\mathrm{Zn}(s)+\mathrm{HgO}(s)+\mathrm{H_2O}(l)\rightarrow \mathrm{Zn(OH)_2}(s)+\mathrm{Hg}(l)$$

The reduction of 1 mol of HgO occurs with the passage of 2 mol of electrons through an outside circuit, that is, Hg(II) is reduced to Hg(0). 0.50 g of $\mathrm{HgO}\left(\mathcal{M}=216.59\ \mathrm{g\ mol^{-1}}\right)$ is 2.3×10^{-3}. Hence, 4.6×10^{-3} mol of electrons must pass the circuit to cause complete discharge. Multiplying by the Faraday constant converts this to $4.5\times10^{2}\mathrm{C}$.

b) The maximum electrical work performed on the battery is

$$w=-\mathcal{Q}\Delta\mathcal{E}=-\left(4.5\times10^{2}\ \mathrm{C}\right)\left(1.34\ \mathrm{V}\right)=-6.0\times10^{2}\ \mathrm{J}$$

The battery can perform at most 600 J of electrical work on its surroundings.

17.56 Partial discharge of the lead-acid battery in the vain effort to start the car reduces the concentration of sulfuric acid in the liquid electrolyte inside the battery. This raises the freezing point (a colligative property) of the electrolyte. After the battery re-cools (it generates some internal heat in the starting effort), the dilute electrolyte freezes despite the somewhat warmer ambient temperature.

17.58 The ΔG^0 for the oxidation of 1.00 mol of $\mathrm{CO}(g)$ to $\mathrm{CO_2}(g)$ is $-257.21\ \mathrm{kJ}$, regardless of how the reaction is performed. If the reaction is performed with 100% efficiency at standard conditions, then $\Delta G^0=w$ and the cell absorbs $-257.21\ \mathrm{kJ}$ of work, that is, –257.21 kJ of work is obtained.

17.60 The standard cell voltage for the rusting of iron according to the overall equation

$$\mathrm{Fe}(s)+\tfrac{1}{2}\mathrm{O_2}(g)+2\ \mathrm{H_3O^+}(aq)\rightarrow \mathrm{Fe^{2+}}(aq)+3\ \mathrm{H_2O}(l)$$

is $\Delta\mathcal{E}^0=\mathcal{E}^0_{\text{cathode}}-\mathcal{E}^0_{\text{anode}}=1.229-(-0.409)=1.638\ \mathrm{V}$. Such a large positive voltage indicates a considerable driving force for the rusting of iron in contact with a water solution at a pH of 0 and oxygen at a pressure of 1 atm. Making the water more acidic increases the driving force.

17.62 The successful use of titanium as a sacrificial anode proves that it is more easily oxidized than iron. Assuming that Ti(*s*) corrodes to Ti^{3+}(*aq*), the standard reduction potential for Ti^{3+} to Ti(*s*) is therefore more negative than –0.409 V, which is the standard potential for the reduction of Fe^{2+}(*aq*) to Fe(*s*).

17.64 At the cathode the potassium ion is reduced: $e^-+\mathrm{K^+}\rightarrow\mathrm{K}$; at the anode, hydroxide ion is oxidized to oxygen: $2\ \mathrm{OH^-}\rightarrow 1/2\ \mathrm{O_2}+\mathrm{H_2O}+2\ e^-$.

17.66 7.0 days is $6.048\times10^{5}\mathrm{s}$. A steady current of 75 000 A for this period means that $4.536\times10^{10}\mathrm{C}$ passes through the circuit. Dividing by the Faraday constant gives the chemical amount of electrons passing through the circuit. It is 4.70×10^{5} mol. Every 2 mol of electrons theoretically accounts for the deposition of 1 mol of Mg. The theoretical yield of Mg is therefore 2.35×10^{5} mol, which is 5.7×10^{6} g.

17.68 If the temperature is high enough to melt the vanadium (m.p. 1890°), as seems likely, the equation is

$$V_2O_5(s) + 5\ Ca(l) \rightarrow 2\ V(l) + 5\ CaO(s)$$

Thus, 5 mol of Ca is required for every 2 mol of V. The 20.0 kg of V is 0.393 kmol of V so 0.982 kmol of Ca is theoretically required. This is 39.3 kg of Ca.

17.70 A current of 1.5 A for 22 minutes means that 1.98×10^3 C, which is 0.0205 mol of electrons, passes the cell. Each mole of electrons deposits one mole of silver on the spoon; since the molar mass of silver is 107.87 g mol^{-1}, this is 2.214 g of silver. The volume of this silver is 0.211 cm^3. This volume of silver covers the 16 cm^2 of spoon surface to an average thickness of 0.013 cm.

17.72 **a)** Anode: $3\ H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2\ H_3O^+(10^{-7}\ M) + 2\ e^-$

Cathode: $2\ H_3O^+(10^{-7}\ M) + 2\ e^- \rightarrow H_2(g) + 2\ H_2O(l)$

b) Using reduction potentials for the above half-reactions

$$\Delta\mathcal{E} = -0.414\ V - 0.815\ V = -1.229\ V$$

The decomposition potential is +1.229 V.

c) Gaseous hydrogen is formed at the cathode

$$m_{H_2} = 50.0\ h\left(\frac{1.50\ C}{s}\right)\left(\frac{3600\ s}{h}\right)\left(\frac{1\ mol\ e^-}{96485\ C}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{2.016\ g\ H_2}{1\ mol}\right) = 2.82\ g\ H_2$$

17.74 The black silver sulfide is reduced while the zinc is oxidized:

$$2\ e^- + Ag_2S(s) + H_2O(l) \rightarrow 2\ Ag(s) + HS^-(aq) + OH^-(aq)$$
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$$

17.76 **a)**

Anode: $Co(s) \rightarrow Co^{2+}(aq) + 2\ e^-$

Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Overall: $Co(s) + 2\ Ag^+(aq) \rightarrow Co^{2+}(aq) + 2\ Ag(s)$

b)

$$\Delta m_{cathode} = \frac{0.36\ g\ Co}{58.93\ g\ mol^{-1}}\left(\frac{2\ mol\ Ag}{1\ mol\ Co}\right)\left(\frac{107.868\ g\ Ag}{1\ mol\ Ag}\right) = 1.32\ g\ Ag$$

c)

$$I = \frac{0.36\ g\ Co}{58.93\ g\ mol^{-1}}\left(\frac{2\ mol\ e^-}{1\ mol\ Co}\right)\left(\frac{96485\ C}{1\ mol\ e^-}\right)\left(\frac{1}{150\ min}\right)\left(\frac{1\ min}{60\ s}\right) = \frac{0.13\ C}{s} = 0.13\ A$$

17.78 The key to the problem is writing a balanced redox equation to represent the reaction by which selenate ion is reduced and water is oxidized. The equation is

$$2\ \mathrm{SeO_4^{2-}}(aq) + 2\ \mathrm{H_2O}(l) \rightarrow 2\ \mathrm{Se}(s) + 3\ \mathrm{O_2}(g) + 4\ \mathrm{OH^-}(aq)$$

It is tempting to focus narrowly on the formula of the selenate ion and reason that 2 mol of $O_2(g)$ must form in the reduction of 1 mol of SeO_4^{2-}. This is wrong because it does not take into account the charge on the selenate ion. The correct ratio is 3/2, as the equation shows.

$$m_{\mathrm{O_2}} = 10^{12}\ \mathrm{L} \times \left(\frac{0.100\ \mathrm{g\ SeO_4^{2-}}}{1\ \mathrm{L}}\right) \times \left(\frac{1\ \mathrm{mol\ SeO_4^{2-}}}{143\ \mathrm{g\ SeO_4^{2-}}}\right) \times \left(\frac{3\ \mathrm{mol\ O_2}}{2\ \mathrm{mol\ SeO_4^{2-}}}\right)$$
$$\times \left(\frac{32.0\ \mathrm{g\ O_2}}{1\ \mathrm{mol\ O_2}}\right) = 3.4 \times 10^{10}\ \mathrm{g\ O_2}$$

17.80 Use a series of unit conversions. The maximum allowable concentration of Sn^{2+} is 10 ppm. Each 100 mL sample of rinse solution has a mass of 100 g because it is a dilute solution and consists mostly of water (density = 1.00 g mL^{-1}). Then:

$$t_{\mathrm{max}} = 100\ \mathrm{mL\ sample} \times \left(\frac{1.00\ \mathrm{g\ sample}}{1.00\ \mathrm{mL}}\right) \times \left(\frac{10 \times 10^{-6}\ \mathrm{g\ Sn^{2+}}}{1\ \mathrm{g\ sample}}\right) \times \left(\frac{1\ \mathrm{mol\ Sn^{2+}}}{118.71\ \mathrm{g\ Sn^{2+}}}\right)$$
$$\times \left(\frac{2\ \mathrm{mol}\ e^-}{1\ \mathrm{mol\ Sn^{2+}}}\right) \times \left(\frac{96485\ \mathrm{C}}{1\ \mathrm{mol}\ e^-}\right) \times \left(\frac{1\ \mathrm{s}}{25.0 \times 10^{-3}\ \mathrm{C}}\right) = 65\ \mathrm{s}$$

17.82 For the reaction $\mathrm{TiCl_4}(l) \rightarrow \mathrm{Ti}(s) + 2\mathrm{Cl_2}(g)$

$$\Delta H^0_{298} = -(-750\ \mathrm{kJ}) = +750\ \mathrm{kJ} \quad \text{and} \quad \Delta S^0_{298} = 30 + 2(223) - 253 = +223\ \mathrm{J\ K^{-1}}$$

At 100°C (373 K) and assuming that $\Delta H^0_{373} = \Delta H^0_{298}$ and $\Delta S^0_{373} = \Delta S^0_{298}$

$$\Delta G^0_{373} = \Delta H^0_{373} - T\Delta S^0_{373} = 750{,}000\ \mathrm{J} - 373\ \mathrm{K}(223\ \mathrm{J\ K^{-1}}) = +666.8\ \mathrm{kJ\ mol^{-1}}$$
$$\Delta \mathcal{E}^0_{373} = -\frac{\Delta G^0_{373}}{n\mathcal{F}} = -\frac{666.8 \times 10^3\ \mathrm{J\ mol^{-1}}}{(4)(96485\ \mathrm{C\ mol^{-1}})} = -1.73\ \mathrm{V}$$

The minimum applied voltage is +1.73 V, assuming that $Cl_2(g)$ is produced at 1 atm.

17.84 In the absence of hydrochloric acid, the $\Delta\mathcal{E}^0$ for the oxidation of Pt by nitric acid is

$$\Delta\mathcal{E}^0 = 0.96 - 1.2\ \mathrm{V} = -0.24\ \mathrm{V} < 0$$

The negative sign shows that the reaction

$$3\ \mathrm{Pt} + 2\ \mathrm{NO_3^-} + 8\ \mathrm{H_3O^+} \rightarrow 3\ \mathrm{Pt^{2+}} + 2\ \mathrm{NO} + 12\ \mathrm{H_2O}$$

is not spontaneous. When hydrochloric acid *is* present (as with aqua regia) the Pt^{2+} can complex with chloride ion. For the reaction

$$3\ \mathrm{Pt} + 12\ \mathrm{Cl^-} + 2\ \mathrm{NO_3^-} + 8\ \mathrm{H_3O^+} \rightarrow 3\ \mathrm{PtCl_4^{2-}} + 2\ \mathrm{NO} + 12\ \mathrm{H_2O}$$

the cell voltage is $\Delta\mathcal{E}^0 = 0.96 - 0.73 = 0.23\ \mathrm{V} > 0$; the reaction can occur spontaneously.

17.86 **a)** The $\Delta\mathcal{E}^0$ for the proposed reduction of $Cu^{2+}(aq)$ by $I^-(aq$ is $(0.158)-(0.535)=-0.377$ V. The reaction of the two ions in their standard states to give $Cu^+(aq)$ and $I_2(s)$ in their standard states is therefore non-spontaneous.

b) Recognize that CuI(*s*) forms. Then the reduction half-reaction in part a) is replaced by another half-reaction with an $\mathcal{E}^0$ of 0.86 V. Now, $\Delta\mathcal{E}^0=(0.86)-(0.535)=0.32$ V. The reaction giving CuI(*s*) in its standard state from aqueous Cu^{2+} and I^- in their standard states *is* spontaneous. The formation of insoluble CuI drives an interaction between the ions that would not occur if the product ions formed in their standard states.

17.88 **a)** Use the Nernst equation at 25°C to calculate the half-cell potential

$$\mathcal{E}=\mathcal{E}^0-\frac{0.0592}{n}\log Q_{\text{hc}}=1.229-\frac{0.0592}{4}\log\left(\frac{1}{P_{O_2}\left[H_3O^+\right]^4}\right)$$

$$=1.229-\frac{0.0592}{4}\log\left(\frac{1}{(1.0)\left(1.0\times10^{-7}\right)^4}\right)=0.815\text{ V}$$

b) Aeration of a solution puts $O_2(g)$ at a partial pressure of about 0.2 atm in contact with the solutes that the solution contains. The reaction

$$O_2(g)+4\ H_3O^+(aq)+4\ I^-(aq)\rightarrow 6\ H_2O(l)+2\ I_2(s)$$

has $\Delta\mathcal{E}^0=0.815-0.535=0.280$ V at pH 7. This means the oxidation of the iodide ion is spontaneous at pH 7 if the pressure of oxygen is 1 atm. The reaction tendency is slightly less at P_{O_2} = 0.2 atm, but the reaction is still spontaneous, as can be confirmed with the Nernst equation:

$$\Delta\mathcal{E}=0.280-\frac{0.0592}{4}\log\frac{1}{P_{O_2}}=0.280-\frac{0.0592}{4}\log\frac{1}{(0.2)}=0.280-0.01=0.27\text{ V}$$

c) The standard reduction potentials of $Br_2(l)$ and $Cl_2(g)$ to Br^- (*aq*) and Cl^- (*aq*) are larger than that of $I_2(s)$. Both exceed 0.815 V, so the $\Delta\mathcal{E}^0$'s for reactions analogous to the aerial oxidation of $I^-(aq)$ are negative. Oxygen from the air is not a sufficiently strong oxidizing agent to take Br^- (*aq*) or $Cl^-(aq)$ to their elemental forms at 1 atm pressure.

d) Decomposition of solutions of I^- by aeration is favored by increasing the H_3O^+ concentration. This makes the denominator of the *Q* term in the Nernst equation larger, and $\Delta\mathcal{E}$ is larger.

17.90 **a)** Both half-cell reactions involve species not in their standard states. The standard reduction potentials for the two have to be corrected to the actual conditions by means of the Nernst equation. Compute the reduction potential for the half-reaction at the anode:

$$\mathcal{E}_{Pb^{2+}/Pb}=\mathcal{E}^0-\frac{0.0592}{2}\log\frac{1}{\left[Pb^{2+}\right]}=-0.1263-\frac{0.0592}{2}\log\frac{1}{1.0\times10^{-2}}=-0.1855\text{ V}$$

The half-reaction involving the lead is written as an oxidation in the problem, but a reduction potential is preferable in computations. This is why the standard reduction potential appears in the above Nernst equation and why Q_{hc} is set up for a reduction. For the cell:

$$\Delta\mathcal{E}=0.640\text{ V}=\mathcal{E}(\text{cathode})-\mathcal{E}(\text{anode})=\mathcal{E}(\text{cathode})-(-0.1855)$$

This means that the reduction potential for the $VO^{2+}|V^{3+}$ half-cell at the cathode is 0.4545 V. This is *not* a standard reduction potential because some of the species in the half-cell are not in their standard states. To compute the standard reduction potential, write the Nernst equation for the VO^{2+}/V^{3+} half-cell:

$$0.4545 = \mathcal{E}^0 - \frac{0.0592}{n}\log\left(\frac{\left[V^{3+}\right]}{\left[VO^{2+}\right]\left[H_3O^+\right]^2}\right) = \mathcal{E}^0 - \frac{0.0592}{1}\log\left(\frac{\left(1.0\times10^{-5}\right)}{\left(0.10\right)\left(0.10\right)^2}\right)$$

Solving gives $\mathcal{E}^0 = 0.336$ V.

b) The chemical equation is the combination of the two half-equations of part a). The standard potential difference is

$$\Delta\mathcal{E}^0 = \mathcal{E}^0(\text{cathode}) - \mathcal{E}^0(\text{anode}) = 0.336 - (-0.1263) = 0.462\ \text{V}$$

Substitute this $\Delta\mathcal{E}^0$ and $n = 2$ into the following expression

$$\log_{10}K_{298} = \frac{n}{0.0592\ \text{V}}\Delta\mathcal{E}^0 \quad \text{from which} \quad K_{298} = 4\times10^{15}$$

17.92

$$Pb(s) \rightarrow Pb^{2+}(aq) + 2\ e^-\ \text{anode} \quad AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)\ \text{cathode}$$

$$\Delta\mathcal{E}^0 = 0.222 - (-0.1263) = 0.3483\ \text{V}$$

$$\Delta\mathcal{E} = 0.546\ \text{V} = \Delta\mathcal{E}^0 - \frac{0.0592}{n}\log Q = 0.3483 - \frac{0.0592}{2}\log\left[Pb^{2+}\right]\left[Cl^-\right]^2$$

Substituting $[Cl^-] = 1.00$ M in this equation gives $\left[Pb^{2+}\right] = 2.1\times10^{-7}$ M in the cell. Use this result in the K_{sp} expression for $PbSO_4(s)$ along with the known concentration of SO_4^{2-} ion

$$K_{sp} = \left[Pb^{2+}\right]\left[SO_4^{2-}\right] = \left(2.1\times10^{-7}\right)\left(0.0500\right) = 1.0\times10^{-8}$$

17.94 The reaction $H_2O(l) \rightarrow H_2(g) + 1/2\ O_2(g)$ begins to occur.

17.96

$$Fe^{2+} + 2e^- \rightarrow Fe(s) \quad \mathcal{E}^0 = -0.409\ \text{V}$$

$$Sn^{2+} + 2e^- \rightarrow Sn(s) \quad \mathcal{E}^0 = -0.1364\ \text{V}$$

$$Zn^{2+} + 2e^- \rightarrow Zn(s) \quad \mathcal{E}^0 = -0.7628\ \text{V}$$

Because Zn^{2+} has a more negative reduction potential, Zn(*s*) is more easily oxidized than Fe(*s*). It therefore protects the Fe from oxidation. This is not true of tin, however; Fe(*s*) dissolves, rather than Sn(*s*), if the coating of tin is broken to expose the iron.

17.98 The standard potential for $K^+ + e^- \rightarrow K(s)$ is –2.925 V. This is much more negative than –0.414 V, which is $\mathcal{E}^0$ for $2\ H_3O^+(10^{-7}\ \text{M}) + 2e^- \rightarrow H_2(g) + 2\ H_2O(l)$. For this reason $H_2(g)$ appears at the cathode.

The $\mathcal{E}^0$ for $Br_2(l)+2e^- \rightarrow 2\ Br^-(aq)$ is 1.065 V. Compute E :

$$\mathcal{E}=\mathcal{E}^0-\frac{0.0592}{n}\log\left[Br^-\right]^2=1.065-\frac{0.0592}{2}\log(0.05)^2=1.142\text{ V}$$

This is more positive than 0.815 V which is $\mathcal{E}^0$ for

$$2\ H_3O^+\left(10^{-7}\text{M}\right)+\tfrac{1}{2}O_2(g)+2e^- \rightarrow 3\ H_2O(l)$$

$O_2(g)$ appears at the anode.

17.100

$$t=55.5\text{ kg crude Cu}\times\left(\frac{98.3\text{ kg Cu}}{100\text{ kg Cu}}\right)\times\left(\frac{1\text{ mol Cu}}{0.063546\text{ kg crude Cu}}\right)\times\left(\frac{2\text{ mol }e^-}{1\text{ mol Cu}}\right)$$
$$\times\left(\frac{96485\text{ C}}{1\text{ mol }e^-}\right)\times\left(\frac{1\text{ s}}{2.00\times10^3\text{ C}}\right)=8.28\times10^4\text{ s}\approx1\text{ d}$$

17.102 The relevant anodic half-reaction is $4\ OH^-(aq) \rightarrow O_2(g)+2\ H_2O+4\ e^-$, and the chemical amount of electrons reacting is

$$n_{e^-}=\frac{\left(0.15\text{ C s}^{-1}\right)\left(75\times60\text{ s}\right)}{\left(96{,}485\text{ C mol}^{-1}\right)}=7.0\times10^{-3}\text{ mol }e^-=7.0\text{ mmol }e^-$$

In the balanced half-equation, 4 mmol e^- is generated per 1 mmol of $O_2(g)$. The amount of oxygen produced is 1/4 of 7.0 mmol, or 1.75 mmol O_2.

At 25°C the partial pressure of water vapor is 0.03126 atm, so the partial pressure of O_2 is $P_{O_2}=0.985-0.03126=0.954\text{ atm}$ and the volume it occupies is

$$V_{O_2}=\frac{n_{O_2}RT}{P_{O_2}}=\frac{(1.75\text{ mmol})\left(0.08206\text{ L atm mol}^{-1}\text{K}^{-1}\right)(298\text{ K})}{0.954\text{ atm}}=45\text{ mL}$$

17.104 To make 1.0 kg of Al by recycling cans, the energy cost is

$$\left(\frac{10.7\text{ kJ mol}^{-1}}{26.98\text{ g mol}^{-1}}\right)\times\left(1000\text{ g kg}^{-1}\right)=400\text{ kJ kg}^{-1}$$

This is only 0.8% of the energy cost of producing the same kilogram of aluminum from its ore.

17.106 a) $I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 2\ I^-(aq) + S_4O_6^{2-}(aq)$

b) $(0.05640\text{ L})(0.100\text{ mol L}^{-1}) = 5.640 \times 10^{-3}\text{ mol }S_2O_3^{2-}$

$$n_{I_2} = 5.640 \times 10^{-3}\text{ mol }S_2O_3^{2-}\left(\frac{1\text{ mol }I_2}{2\text{ mol }S_2O_3^{2-}}\right) = 2.82 \times 10^{-3}\text{ mol }I_2$$

c) For $I_2(s) + 2\ S_2O_3^{2-}(aq) \rightleftharpoons 2\ I^-(aq) + S_4O_6^{2-}(aq) \quad \Delta\mathcal{E}^0 = 0.535 - 0.0895\text{ V} = 0.4455\text{ V}$

$$\log_{10}K_1 = \frac{n}{0.0592}\Delta\mathcal{E}^0 = \frac{2}{0.0592}(0.4455) = 15.05 \qquad \text{so that} \qquad K_1 = 1 \times 10^{15}$$

For $I_2(aq) \rightleftharpoons I_2(s)$

$$\Delta G^0 = 0 - 16.40\text{ kJ} = -16.40\text{ kJ} \qquad \text{so that} \qquad K_2 = \exp\left(-\frac{\Delta G^0}{RT}\right) = 7.5 \times 10^2$$

The reaction in part **a)** is the sum of these two reactions so

$$K = K_1K_2 = 8 \times 10^{17}$$

Chapter 18

Chemical Kinetics

18.2 The rate of the reaction at t = 100 s is the slope of a straight line that is tangent to the blue curve in Figure 18.3 at the point where it intersects the vertical line labelled 100 s. This straight line passes through the points (0.0300, 150) and (0.0125, 0). Its slope is $(0.0300-0.0125)/(150-0)=1.17\times10^{-4}$ mol L^{-1}s^{-1}.

18.4 The expressions are

$$\text{rate}=-\frac{1}{2}\frac{d[H_2CO]}{dt}=-\frac{d[O_2]}{dt}=+\frac{1}{2}\frac{d[CO]}{dt}=+\frac{1}{2}\frac{d[H_2O]}{dt}$$

18.6 **a)** The rate equation is

$$\text{rate}=k[SO_2][SO_3]^{-1/2}=k\frac{[SO_2]}{[SO_3]^{1/2}}$$

The reaction is one-half order overall so the units of k are mol$^{1/2}$L$^{-1/2}$s^{-1}.
b) The accelerating effect of the larger concentration of SO_2 is exactly offset by the decelerating effect of the larger concentration of SO_3. The rate does not change.

18.8 **a)** Increasing the concentration of Fe^{2+} by a factor of 1.6 between the first and second experiments (while the concentration of Ce^{4+} is constant) increases the rate by a factor of 1.6; the reaction is first-order in Fe^{2+}. Increasing the concentration of Ce^{4+} by a factor of 3.1 between the second and third experiments (while the concentration of Fe^{2+} stays constant) increases the rate by a factor of 3.1; the reaction is first-order in Ce^{4+}. The rate law is rate $=\kappa[Fe^{2+}][Ce^{4+}]$.

b) Substitute one of the three sets of data into the rate law. The first set gives:

$$2.0\times10^{-7}\text{ mol L}^{-1}\text{s}^{-1}=\kappa(1.8\times10^{-5}\text{ mol L}^{-1})(1.1\times10^{-5}\text{ mol L}^{-1})$$

From this, $\kappa=1.0\times10^{3}$ L mol^{-1}s^{-1}. The other two sets of data give the same κ (to two significant figures).

c) Substitute the given concentrations and the κ from part **b)** into the rate law. The initial rate should be 3.4×10^{-7} mol L^{-1}s^{-1}.

18.10 **a)** The half-life of a first-order process is In 2 (0.6931) divided by the first-order rate constant.
The answer is 1.03×10^{3}s.

b) A quick answer comes by noting that 0.010 atm is $\frac{1}{4}$ of the original pressure of 0.040 atm. The pressure drops to half its original value in the first half-life and to half of that in a second half-life. The answer is two half-lives, or 2.1×10^{3} s.

More generally, write the integrated first order rate law for this reaction at 322°C

$$\frac{[FClO_2]}{[FClO_2]_0} = e^{-(6.76\times10^{-4}\,s^{-1})t}$$

and solve for t

18.12 The partial pressure of the $CH_3CH_2NO_2(g)$ changes with time according to

$$\ln P = -\kappa t + \ln P_0$$

assuming that its partial pressure is directly proportional to its concentration. Substituting gives

$$\ln P = -(1.9\times10^{-4}\,s^{-1})(1.08\times10^{4}\ s) + \ln 0.078 = -4.603 \quad \text{and} \quad P = 0.010\ \text{atm}$$

18.14 The concentration of the CH_3NC diminishes to 0.71 of its original value in 520 s in a first-order process.

$$\ln(0.71) = -\kappa t = \kappa(520\ s) \quad \text{from which} \quad \kappa = 6.6\times10^{-4}\,s^{-1}$$

18.16 The disappearance of the HO_2 is second order in the concentration of HO_2.

$$\frac{1}{[HO_2]} - \frac{1}{[HO_2]_0} = 2\kappa t$$

$$\frac{1}{[HO_2]} - \frac{1}{2\times10^{-8}\ \text{mol L}^{-1}} = 2(1.4\times10^{9}\ \text{L mol}^{-1})t$$

Solve for $[HO_2]$ at t = 1.0 s. the result is 3.5×10^{-10} mol L^{-1}.

18.18 The concentrations of the OH^- (aq) and the HCN(aq) start at 0.0010 mol L^{-1} and stay equal to each other during the course of the reaction. Let their original concentration be x_0 and their concentration at any later time be x. Then

$$\text{Rate} = -\frac{d[OH^-]}{dt} = \kappa[OH^-][HCN] \quad \text{gives} \quad -\frac{dx}{dt} = \kappa x^2 \quad \text{which gives} \quad -\frac{dx}{x^2} = \kappa dt$$

Integration and evaluation followed by substitution give

$$\frac{1}{x} - \frac{1}{x_0} = \kappa t \ \text{ then } \ \frac{1}{0.00010\ \text{mol L}^{-1}} - \frac{1}{0.0010\ \text{mol L}^{-1}} = (3.7\times10^{9}\ \text{L mol}^{-1}\text{s}^{-1})t$$

Solving gives $t = 2.4\times10^{-6}$ s.

18.20 **a)** Unimolecular, rate = $\kappa[BrONO_2]$.
b) Termolecular, rate = $\kappa[HO][NO_2][Ar]$.
c) Bimolecular, rate = $\kappa[O][H_2S]$.

18.22 **a)** Each of the steps in a mechanism must be an elementary reaction. Therefore, the molecularity of the three steps given here is just the number of species on the left of the arrow: 1, 2, and 3, respectively.

b) The equation is $NO_2Cl + H_2O \rightarrow HNO_3 + HCl$.

c) The intermediates are the species in this mechanism that are created in one step of the reaction and consumed in another: NO_2, Cl, OH.

18.24 The equilibrium constant for the mer $\rightleftharpoons$ fac reaction is K = [fac]/[mer]. At equilibrium the rate of the mer → fac reaction equals the rate of the fac → mer reaction. Then $2.10\ \text{s}^{-1}[\text{fac}] = 2.33\ \text{s}^{-1}[\text{mer}]$. Solving for the ratio [fac]/[mer] gives $K = 1.11$.

18.26 **a)** For $2\text{A} + 2\text{B} \rightarrow \text{E} + \text{G}$ the rate law is: rate = $\kappa_2[\text{D}][\text{B}] = K_1\kappa_2[\text{A}]^2[\text{B}]^2$ according to the mechanism given.

b) The reaction $\text{A} + \text{B} + \text{D} \rightarrow \text{G}$ has the rate law:

$$\text{rate} = \kappa_3[\text{F}] = \kappa_3 K_2[\text{C}][\text{D}] = \kappa_3 K_2 K_1[\text{A}][\text{B}][\text{D}]$$

according to the mechanism given.

18.28 The mechanism **a)**, which starts with a rate-determining collision between $Cl_2(aq)$ and $H_2S(aq)$, is consistent with the observed rate law: rate = $K_1[Cl_2][H_2S]$ According to the second mechanism, the rate would be

$$\text{rate} = \kappa_2[\text{Cl}_2][\text{HS}^-] = \kappa_2 K_1[\text{Cl}_2]\frac{[\text{H}_2\text{S}]}{[\text{H}^+]}$$

Thus, the reaction would still be first order in both $Cl_2(aq)$ and $H_2S(aq)$, but -1 order in $H^+(aq)$ and therefore only first order overall. This does not fit the stated facts. According to the third mechanism, the reaction would be first order in both $Cl_2(aq)$ and $H_2S(aq)$, but -1 order in $H^+(aq)$ and also -1 order in Cl^- (aq) and therefore zero order overall.

18.30 Both mechanisms **a)** and **b)** predict the experimentally found rate expression. Mechanism **c)** predicts that the reaction would be second order in NO_2 and first order in O_3, and is not acceptable.

18.32

$$\frac{d[\text{C}]}{dt} = \kappa_1[\text{A}] - \kappa_{-1}[\text{B}][\text{C}] - \kappa_2[\text{C}][\text{D}] + \kappa_{-2}[\text{E}] = 0$$

$$\frac{d[\text{E}]}{dt} = \kappa_2[\text{C}][\text{D}] - \kappa_{-2}[\text{E}] - \kappa_3[\text{E}] = 0$$

$$[\text{E}] = \frac{\kappa_2[\text{C}][\text{D}]}{\kappa_{-2} + \kappa_3}$$

Substituting in the first equation gives

$$\kappa_1[\mathrm{A}]-\kappa_{-1}[\mathrm{B}][\mathrm{C}]-\kappa_2[\mathrm{C}][\mathrm{D}]-\frac{\kappa_{-2}\kappa_2}{\kappa_{-2}+\kappa_3}[\mathrm{C}][\mathrm{D}]=0$$

$$[\mathrm{C}]=\frac{\kappa_1[\mathrm{A}]}{\kappa_{-1}[\mathrm{B}]+\left(\kappa_2+\frac{\kappa_{-2}\kappa_2}{\kappa_{-2}+\kappa_3}\right)[\mathrm{D}]}$$

$$[\mathrm{E}]=\frac{\kappa_1\kappa_2[\mathrm{A}][\mathrm{D}]}{\kappa_{-1}(\kappa_{-2}+\kappa_3)[\mathrm{B}]+\kappa_2(2\kappa_{-2}+\kappa_3)[\mathrm{D}]}$$

$$\mathrm{Rate}=\kappa_3[\mathrm{E}]=\frac{\kappa_1\kappa_2\kappa_3[\mathrm{A}][\mathrm{D}]}{\kappa_{-1}(\kappa_{-2}+\kappa_3)[\mathrm{B}]+\kappa_2(2\kappa_{-2}+\kappa_3)[\mathrm{D}]}$$

This reduces to the result of problem 13-25b if $\kappa_3 << \kappa_{-2}$ and $\kappa_2[\mathrm{D}] << \kappa_{-1}[\mathrm{B}]$.

18.34 According to the steady-state approximation,

$$\frac{d[\mathrm{SO_2OOH^-}]}{dt}=\kappa_1[\mathrm{HSO_3^-}][\mathrm{H_2O_2}]-\kappa_{-1}[\mathrm{SO_2OOH^-}]-\kappa_2[\mathrm{SO_2OOH^-}][\mathrm{H_3O^+}]=0$$

Solving for the concentration of SO_2OOH^- gives

$$[\mathrm{SO_2OOH^-}]=\frac{\kappa_1[\mathrm{HSO_3^-}][\mathrm{H_2O_2}]}{\kappa_{-1}+\kappa_2[\mathrm{H_3O^+}]}$$

so that the reaction rate is

$$\mathrm{rate}=\kappa_2[\mathrm{SO_2OOH^-}][\mathrm{H_3O^+}]=\frac{\kappa_1\kappa_2[\mathrm{HSO_3^-}][\mathrm{H_2O_2}][\mathrm{H_3O^+}]}{\kappa_{-1}+\kappa_2[\mathrm{H_3O^+}]}$$

18.36 According to the Arrhenius equation, the logarithm of the rate constant is a linear function of the reciprocal of the absolute temperature with a slope of $-E_a/R$ and an intercept of In *A*.

a) Most students will use the Arrhenius equation with various pairs of the six data given and compute varied answers, because there is some experimental scatter to the points. The best way to use all of the data is to perform a linear least-square fit of ln κ versus $1/T$. The slope of the line is −4360 K, and the intercept is 23.962. This means that $E_a=-(-4360\ \mathrm{K})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})=36{,}200\ \mathrm{J\ mol^{-1}}$.

b) The constant *A* is the exponential of the intercept from part **a)**. It always has the same units as κ: $A=2.6\times10^{10}\ \mathrm{s^{-1}}$.

18.38 **a)** Let *x* represent the partial pressure of N_2O_4. The reaction is first order in *x*, hence

$$-\ln\frac{x}{x_0}=\kappa t \text{ from which } -\ln\frac{0.010\ \mathrm{atm}}{0.10\ \mathrm{atm}}=(5.1\times10^6\mathrm{s^{-1}})t \text{ and } \mathrm{t}=4.5\times10^{-7}\ \mathrm{s}$$

b) Figure the rate constant κ at 573.15 K using the Arrhenius equation

$$\ln\frac{\kappa_{573}}{5.1\times10^6\mathrm{s^{-1}}}=\frac{-54.0\times10^3\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}}\left[\frac{1}{573.15\ \mathrm{K}}-\frac{1}{303.15\ \mathrm{K}}\right]$$

$$\kappa_{573}=1.2\times10^{11}\mathrm{s^{-1}}$$

Repeat the calculation of part a) using this bigger κ

$$-\ln\frac{0.010\text{ atm}}{0.10\text{ atm}}=\left(1.2\times10^{11}\text{s}^{-1}\right)t\text{ and }t=1.9\times10^{-11}\text{s}$$

18.40 **a)** The Arrhenius equation gives *In A* in terms of κ, T, and E_a, which are stated explicitly in the problem:

$$\ln A=\ln\kappa+\frac{E_a}{RT}=\ln\left(6.1\times10^{-4}\right)+\frac{272{,}000\text{ J mol}^{-1}}{\left(8.3145\text{ J mol}^{-1}\text{ K}^{-1}\right)\left(773\text{ K}\right)}=34.9$$

Hence $A=1.5\times10^{15}\text{s}^{-1}$. Note that the units of A are always the same as the units of κ. Also, the units in the activation energy term cancel out completely.

b) Writing the Arrhenius equation at the two temperatures and taking the ratio gives

$$\ln\frac{\kappa_{773}}{\kappa_{298}}=-\frac{272{,}000\text{ J}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{773\text{ K}}-\frac{1}{298\text{ K}}\right)$$

The ratio $\kappa_{773}/\kappa_{298}$ equals 2×10^{29}, and κ_{773} is given. Therefore $\kappa_{298}=3.1\times10^{-33}\text{s}^{-1}$.

The reaction is very slow at room conditions.

18.42 The ΔE for the $HOCl\rightarrow HClO$ conversion should equal the activation energy for the forward reaction minus the activation energy for the reverse reaction, or $311-31=280\text{ kJ mol}^{-1}$.

18.44 The preexponential factor is

$$2d^2N_A\sqrt{\frac{\pi RT}{\mathcal{M}}}P$$

Substituting d = 2.6 × 10^{-10}m, N_A = 6.022 × 10^{23} mol^{-1}, R = 8.3145 J K^{-1} mol^{-1}, T = 500 K, $\mathcal{M}=46.01\times10^{-3}$ kg mol^{-1}, and $P=5.0\times10^{-2}$ gives

$$2.2\times10^{6}\text{ m}^3\text{ mol}^{-1}\text{s}^{-1}=2.2\times10^{9}\text{ L mol}^{-1}\text{s}^{-1}.$$

18.46 The large rate constant value entails that this reaction is diffusion controlled.

18.48 **a)** The enzyme is carbonic anhydrase and the substrate is carbon dioxide. Write the Michaelis-Menten rate equation (text equation 18.8), letting E stand for carbonic anhydrase

$$\frac{d\left[CO_2\right]}{dt}=\frac{\kappa_2\left[E\right]_0\left[CO_2\right]}{\left[CO_2\right]+K_m}$$

The rate of the reaction is maximized by a large concentration of CO_2. If $[CO_2]$ >> K_m, then the preceding equation becomes

$$\frac{d\left[CO_2\right]}{dt}=\kappa_2\left[E\right]_0$$

Inserting the given values for κ_2 and the concentration of the enzyme gives

$$\frac{d\left[CO_2\right]}{dt}=\left(6\times10^{5}\text{s}^{-1}\right)\left(5\times10^{-6}\text{ mol L}^{-1}\right)=3\text{ mol L}^{-1}\text{ s}^{-1}$$

b) Rewrite text equation 18.8 for this reaction and substitute in it

$$\frac{d[CO_2]}{dt} = \frac{\kappa_2[E]_0[CO_2]}{[CO_2]+K_m}$$

$$.30(3\text{ mol L}^{-1}\text{s}^{-1}) = \frac{(6\times10^5\text{ s}^{-1})(5\times10^{-6}\text{ mol L}^{-1})[CO_2]}{[CO_2]+(8\times10^{-5}\text{ mol L}^{-1})}$$

Solve for $[CO_2]$

$$0.30 = \frac{[CO_2]}{[CO_2]+(8\times10^{-5}\text{ mol L}^{-1})}$$

$$\frac{1}{0.30} = \frac{[CO_2]+(8\times10^{-5}\text{ mol L}^{-1})}{[CO_2]}$$

$$3.33 = 1+\frac{8\times10^{-5}\text{ mol L}^{-1}}{[CO_2]}$$

$$[CO_2] = 3.4\times10^{-5}\text{ mol L}^{-1}$$

18.50 This problem treats an instance of competing reactions reported in the literature (Inorg. Chem. **26** 948 (1987)).

a) The thiosulfate ion and hydrogen peroxide interact in two different ways. Let x be the initial rate of disappearance of $S_2O_3^{2-}$ by the first reaction and let $2y$ be the initial rate of disappearance $S_2O_3^{2-}$ by the second reaction. Then $4x$ is the rate of disappearance of H_2O_2 by the first reaction and y is the rate of disappearance of H_2O_2 by the second reaction. These relationships follow from the stoichiometry. It is now possible to write:

$$x+2y = 7.9\times10^{-7}\text{ mol L}^{-1}\text{ s}^{-1} \quad\text{and}\quad 4x+y = 8.8\times10^{-7}\text{ mol L}^{-1}\text{s}^{-1}$$

because the total rates of disappearance of the reactants are the sums of the rates via the different routes. Solving gives

$$x = 1.386\times10^{-7}\text{mol L}^{-1}\text{s}^{-1} \quad\text{and}\quad y = 3.257\times10^{-7}\text{ mol L}^{-1}\text{s}^{-1}$$

The percentage of $S_2O_3^{2-}$ reacting at the first moment according to the first equation is the rate x divided by total rate of disappearance of $S_2O_3^{2-}$ times 100%. It is 18%.

b) The first reaction generates H_3O^+ at the initial rate *2x,* but the second reaction consumes H_3O^+ at the initial rate 2*y*. The net rate of consumption of H_3O^+ is

$$2y-2x = 3.742\times10^{-7}\text{mol L}^{-1}\text{s}^{-1}$$

This rate is also the initial rate at which replacement H_3O^+ has to be added to keep the pH at 7.0. The volume of the solution to which it is added is 2.00 L, so 7.484 × 10^{-7} mol s^{-1} of H_3O^+ has to be added. In 60 s, this amounts to 4.49 × 10^{-5} mol. This much H_3O^+ is contained in 0.45 mL of 0.100 M H_3O^+.

18.52 **a)** The initial partial pressure (the pressure at time 0) of DTBP is 0.2362 atm. If it has decreased by x atm at time t, to a value of 0.2362 - x atm, then the total pressure of the gas mixture at time t is 0.2362 + $2x$. Then

$$P_{tot} = 0.2362 + 2x \text{ atm so } x = \tfrac{1}{2}P_{tot} - 0.1181 \text{ atm}$$

The expression for the partial pressure of DTBP is

$$P_{DTBP} = 0.2362 - x = 0.2362 - \left(\tfrac{1}{2}P_{tot} - 0.1181\right) = 0.3543 - \tfrac{1}{2}P_{tot}\text{atm}$$

The following table shows the computed values for the pressure of DTBP based on the total pressure at the various times:

time (s)	P_{DTBP} (atm)	time (s)	P_{DTBP} (atm)
0	0.2362	26	0.1882
2	0.2310	30	0.18185
6	0.22365	34	0.1758
10	0.2158	38	0.16995
14	0.20875	40	0.16685
18	0.20175	42	0.16425
20	0.1982	46	0.15885
22	0.1949		

b) The partial pressure of DTBP and its concentration are in direct proportion. If the reaction is first order in DTBP, then, over any set period of time, the natural logarithm of the DTBP pressure will always change by the same amount. If the reaction is second order in DTBP, then, instead of ln P_{DTBP}, $1/P_{DTBP}$ will exhibit a constant change over equal time intervals. The interval of 4 minutes is common in the table. From 2 to 6 minutes $\Delta\left(1/P_{DTBP}\right)$ is 0.1423; from 42 to 46 minutes, it is 0.2070. This is a substantial alteration. For the same pair of intervals $\Delta\left(\ln P_{DTBP}\right) = -0.0323$ and -0.0334. This is very little change. The reaction is first order in DTBP. The same result is obtained by plotting the full set of data as in text Figure 18.8.

18.54 The forward rate of the reaction and the reverse rate of the reaction are

$$\text{rate}_f = \kappa_f P_{CO_2} P^2_{NH_3} \quad \text{and} \quad \text{rate}_r = \kappa_r$$

The net rate is the forward rate minus the reverse rate. At equilibrium the net rate is zero. Hence

$$\kappa_f P_{CO_2} P^2_{NH_3} = \kappa_r \quad \text{and} \quad \frac{\kappa_f}{\kappa_r} = \frac{1}{P_{CO_2} P^2_{NH_3}}$$

But the expression on the right is the equilibrium constant, so $K = \kappa_f/\kappa_r$. Substitution of the two κ's gives $K = 1.49 \times 10^6$.

18.56 **a)** At equilibrium, $\frac{[B]}{[A]} = \frac{\kappa_1}{\kappa_{-1}}$ and $\frac{[C]}{[A]} = \frac{\kappa_2}{\kappa_{-2}}$. Dividing the second expression by the first gives

$$\frac{[C]}{[B]} = \frac{\kappa_2\kappa_{-1}}{\kappa_{-2}\kappa_1} = \frac{\left(1\times10^9\right)\left(1\times10^2\right)}{\left(1\times10^4\right)\left(1\times10^8\right)} = 0.1 = K$$

The ratio of [B] to [C] is the inverse of this, or 10.
b) If κ_{-1} and κ_{-2} can be ignored, then B forms at a rate κ_1/κ_2 times that of C. In this case,

$$\frac{[\mathrm{B}]}{[\mathrm{C}]}=\frac{\kappa_1}{\kappa_2}=\frac{1\times10^8}{1\times10^9}=0.1$$

18.58 The reaction and rate expression are

$$\mathrm{N_2O_5}\rightarrow 2\,\mathrm{NO_2}+\tfrac{1}{2}\mathrm{O_2}\quad \text{rate}=\frac{1}{2}\frac{d[\mathrm{NO_2}]}{dt}=\frac{\kappa_1\kappa_2[\mathrm{M}]}{\kappa_2\kappa_{-1}[\mathrm{M}]}[\mathrm{N_2O_5}]=\kappa_{\text{eff}}[\mathrm{N_2O_5}]$$

The excess N_2 mentioned in the problem is neither consumed nor produced by the reaction, but does take part in the mechanism. It is most of the M. The reciprocal of κ_{eff} is;

$$\frac{1}{\kappa_{\text{eff}}}=\frac{\kappa_2+\kappa_{-1}[\mathrm{M}]}{\kappa_1\kappa_2[\mathrm{M}]}=\frac{\kappa_2}{\kappa_1\kappa_2}\frac{1}{[\mathrm{M}]}+\frac{\kappa_{-1}}{\kappa_1\kappa_2}$$

This shows that $1/\kappa_{\text{eff}}$ is a linear function of 1/[M]. A plot of κ_{eff}^{-1} against P^{-1} based on the data in the problem is also linear. Using least squares, the intercept of the line is 3.316 s, that is,

$$\frac{\kappa_{-1}}{\kappa_1\kappa_2}=3.316\ \text{s}\quad \text{from which}\quad \frac{\kappa_1\kappa_2}{\kappa_{-1}}=0.302\ \text{s}^{-1}$$

This is κ_{eff} at high pressure, when the reaction is first order, as shown in text Section 18.4. The slope of the least-square line in the plot of κ_{eff}^{-1} versus P^{-1} is 3.321 atm s. The slope equals $1/\kappa_1$, the rate constant at low pressure, when the reaction is second order. Converting from pressure to concentration using P/RT = [M] gives

$$\kappa_1=\frac{1}{3.321\ \text{atm s}}\left(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1}\right)\left(300\ \text{K}\right)=7.4\ \text{L mol}^{-1}\text{s}^{-1}$$

18.60 **a)**

$$\frac{d[\mathrm{H}]}{dt}=\kappa_2[\mathrm{Br}][\mathrm{H_2}]-\kappa_4[\mathrm{HBr}][\mathrm{H}]-\kappa_3[\mathrm{H}][\mathrm{Br_2}]$$

b)

$$\frac{d[\mathrm{Br}]}{dt}=2\,\kappa_1[\mathrm{Br_2}][\mathrm{M}]-2\,\kappa_{-1}[\mathrm{Br}]^2[\mathrm{M}]-\kappa_2[\mathrm{Br}][\mathrm{H_2}]+\kappa_4[\mathrm{HBr}][\mathrm{H}]+\kappa_3[\mathrm{H}][\mathrm{Br_2}]$$

Note that 2 κ_1 and 2 κ_{-1} appear because two Br atoms are formed from each Br_2 molecule.

c) Setting the two derivatives to zero and adding gives

$$2\,\kappa_1[\mathrm{Br_2}][\mathrm{M}] - 2\,\kappa_{-1}[\mathrm{Br}]^2[\mathrm{M}] = 0$$

$$[\mathrm{Br}] = \sqrt{\frac{\kappa_1[\mathrm{Br_2}][\mathrm{M}]}{\kappa_{-1}[\mathrm{M}]}} = \sqrt{\frac{\kappa_1}{\kappa_{-1}}}[\mathrm{Br_2}]^{1/2}$$

Setting $\frac{d[\mathrm{H}]}{dt} = 0$ and solving for [H] gives

$$[\mathrm{H}] = \frac{\kappa_2[\mathrm{Br}][\mathrm{H_2}]}{\kappa_4[\mathrm{HBr}] + \kappa_3[\mathrm{Br_2}]} = \frac{\kappa_2(\kappa_1/\kappa_{-1})^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{\kappa_4[\mathrm{HBr}] + \kappa_3[\mathrm{Br_2}]}$$

d)

$$\begin{aligned}\frac{d[\mathrm{HBr}]}{dt} &= \kappa_2[\mathrm{Br}][\mathrm{H_2}] + \kappa_3[\mathrm{H}][\mathrm{Br_2}] - \kappa_4[\mathrm{HBr}][\mathrm{H}] \\ &= \kappa_2(\kappa_1/\kappa_{-1})^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2} + \frac{\kappa_3[\mathrm{Br_2}] - \kappa_4[\mathrm{HBr}]}{\kappa_3[\mathrm{Br_2}] + \kappa_4[\mathrm{HBr}]}\kappa_2(\kappa_1/\kappa_{-1})^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2} \\ &= \frac{2\,\kappa_3\kappa_2(\kappa_1/\kappa_{-1})^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{\kappa_3[\mathrm{Br_2}] + \kappa_4[\mathrm{HBr}]}\end{aligned}$$

18.62 According to mechanism (a)

$$\kappa_1 = \frac{[\mathrm{Fe^{3+}}][\mathrm{Cl^-}][\mathrm{Cl}]}{[\mathrm{Fe^{2+}}][\mathrm{Cl_2}]}$$

and the rate of the reaction (which equals the rate of the slow step) is

$$\frac{d[\mathrm{Fe^{3+}}]}{dt} = \kappa_2[\mathrm{Fe^{2+}}][\mathrm{Cl}] = \kappa_2 K_1 \frac{[Fe^{2+}]^2[\mathrm{Cl_2}]}{[\mathrm{Cl^-}][\mathrm{Fe^{3+}}]}$$

This rate would decrease with increasing [Cl^-] or [Fe^{3+}], which would account for the observations that are cited.

According to mechanism (b)

$$K_3 = \frac{\kappa_3}{\kappa_{-3}} = \frac{[\mathrm{Fe(IV)}][\mathrm{Cl^-}]^2}{[\mathrm{Fe^{2+}}][\mathrm{Cl}]}$$

and

$$\text{rate} = \kappa_4[\mathrm{Fe(IV)}][\mathrm{Fe^{2+}}] = \kappa_4 K_3 \frac{[\mathrm{Fe^{2+}}]^2[\mathrm{Cl_2}]}{[\mathrm{Cl^-}]^2}$$

This rate is independent of [Fe^{3+}] and thus not in accord with the facts.

18.64 a)

$$\kappa_f[A][B] = \kappa_r[C][D] \quad \text{hence} \quad \frac{\kappa_f}{\kappa_r} = \frac{[C][D]}{[A][B]} = K \text{ at equilibrium}$$

b) For an exothermic reaction, K decreases with increasing temperature. Since the reaction is exothermic, the activation energy E_a for the reverse reaction is greater than E_a for the forward reaction. This means that κ_r varies more rapidly with temperature than does κ_f, although both increase with increasing temperature. Since $K = \kappa_f/\kappa_r$, as the temperature increases, the denominator increases more rapidly than the numerator, so K decreases.

18.66 The logarithm of the rate constant κ is a linear function of the reciprocal of the absolute temperature. The slope of this line on an Arrhenius plot is $-E_a/R$. Converting the Celsius temperatures to Kelvin temperatures and performing a least-squares fit (the best way to use all four data points, see solution to problem 13.36) gives slope = -7606.6 K, and therefore E_a = 63.2 kJ mol^{-1}.

18.68 a) Let the ratio of the rates at 308 K and 298 K be x. Then, in the Arrhenius equation:

$$\ln x = \frac{-53{,}000 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{308 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

Solving gives $x = 2.00$.

b) A similar substitution in the Arrhenius equation gives:

$$\ln x = \frac{-53{,}000 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{408 \text{ K}} - \frac{1}{398 \text{ K}}\right)$$

Solving gives $x = 1.48$, which is 1.5.

18.70 a) The reactants are A_2, B, and CD, and the products are AC and BD. The balanced equation is $A_2 + 2\text{ B} + 2\text{ CD} \rightarrow 2\text{ AC} + 2\text{ BD}$. Note that the second step occurs twice as often as the first.

b) $\text{Rate} = \kappa_3[AB][CD] = \kappa_3 K_2[A][B][CD] = \kappa_3 K_2 K_1^{1/2}[A_2]^{1/2}[B][CD]$.

c) Because the first two steps are endothermic, K_1 and K_2 must increase with temperature. This is also true for any elementary reaction rate constant such as κ_3. The result is to increase the overall reaction rate constant.

18.72

$$\frac{d[Ag^{2+}]}{dt} = \kappa_1[Ag^+][Ce^{4+}] - \kappa_{-1}[Ag^{2+}][Ce^{3+}] - \kappa_2[Tl^+][Ag^{2+}] = 0$$

$$[Ag^{2+}] = \frac{\kappa_1[Ag^+][Ce^{4+}]}{\kappa_{-1}[Ce^{3+}] + \kappa_2[Tl^+]}$$

$$\text{Rate} = \kappa_2[Tl^+][Ag^{2+}] = \frac{\kappa_1\kappa_2[Ag^+][Ce^{4+}][Tl^+]}{\kappa_{-1}[Ce^{3+}] + \kappa_2[Tl^+]}$$

18.74 The maximum rate is $\kappa_2[E]_0$, so

$$1\times10^{-6}\text{mol L}^{-1}\text{s}^{-1} = \kappa_2\left(2\times10^{-6}\text{ mol L}^{-1}\right) \quad \text{from which} \quad k_2 = 0.5$$

$$\frac{\text{rate}}{\text{max rate}} = \frac{1}{2} = \frac{[S]}{[S]+K_m}$$

Inserting $[S] = 6\times10^{-6}$ M and solving for K_m gives $K_m = 6\times10^{-6}$ mol L^{-1}.

18.76 Acid-base equilibria are rapidly established, so

$$[H_3O^+] = K_a\frac{[HCN]}{[CN^-]} = \left(6.17\times10^{-10}\right)\left(\frac{0.095\text{ M}}{0.17\text{ M}}\right) = 3.45\times10^{-10}\text{M}$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = 2.9\times10^{-5}\text{ M}$$

$$\text{rate} = k[ClO_2]^2[OH^-]$$

$$= \left(230\text{ L}^2\text{ mol}^{-2}\text{s}^{-1}\right)\left(0.020\text{ mol L}^{-1}\right)^2\left(2.9\times10^{-5}\text{ mol L}^{-1}\right) = 2.7\times10^{-6}\text{ mol L}^{-1}\text{ s}^{-1}$$

18.78 The rms velocity of NO_2 molecules at 400 K is

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}} = \sqrt{\frac{3\left(8.3145\text{ J K}^{-1}\text{ mol}^{-1}\right)\left(400\text{ K}\right)}{0.046005\text{ Kg mol}^{-1}}} = 466\text{ m s}^{-1}$$

For an NO_2 molecule having kinetic energy E_a/N_A where E_a is 111 kJ mol^{-1}

$$\tfrac{1}{2}mu^2 = \frac{E_a}{N_A}$$

$$u^2 = \frac{2\,E_a}{mN_A} = \frac{2E_a}{\mathcal{M}}$$

$$u = \sqrt{\frac{2\,E_a}{\mathcal{M}}} = \sqrt{\frac{2\left(111\times10^3\text{J mol}^{-1}\right)}{0.046005\text{ kg mol}^{-1}}}$$

$$= 2197\text{ m s}^{-1} \approx 2200\text{ m s}^{-1}$$

This exceeds the rms velocity at 400 K by a factor of 4.7

Chapter 19

Nuclear Chemistry

19.2 The nuclear reaction is ${}^{10}_{4}\text{Be} \rightarrow {}^{10}_{5}\text{B} + {}^{0}_{-1}e^{-} + \bar{\nu}$. The kinetic energy of the ${}^{0}_{-1}e^{-}$ is a maximum when the antineutrino has zero kinetic energy: essentially all of the ΔE of the reaction is then carried away by the ${}^{0}_{-1}e^{-}$. The ΔE is $c^2\,\Delta m$, and $\Delta m = -0.0005967$ u, so $\Delta E = -0.556$ MeV. The maximum energy (E_{max} in text Figure 19.3) of the ${}^{0}_{-1}e^{-}$ is +0.556 MeV. Remember that the mass of the ${}^{0}_{-1}e^{-}$ is *not* added in calculating Δm.

19.4 **a)** ${}^{155}_{70}\text{Yb} \rightarrow {}^{151}_{68}\text{Er} + {}^{4}_{2}\text{He}$ **b)** ${}^{26}_{14}\text{Si} \rightarrow {}^{26}_{13}\text{Al} + {}^{0}_{1}e^{+} + \nu$

c) ${}^{65}_{30}\text{Zn} + {}^{0}_{-1}e^{-} \rightarrow {}^{65}_{29}\text{Cu} + \nu$ **d)** ${}^{100}_{41}\text{Nb} \rightarrow {}^{100}_{42}\text{Mo} + {}^{0}_{-1}e^{-} + \bar{\nu}$

19.6 ${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{-1}e^{+}$ ${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}e^{-}$

Alpha emission by ${}^{14}_{6}\text{C}$ would yield ${}^{10}_{4}\text{Be}$ ${}^{14}_{6}\text{C} \rightarrow {}^{10}_{4}\text{Be} + {}^{4}_{2}\text{He}$. This is not a spontaneous process because $\Delta m = 0.0129 \text{ u} > 0$.

19.8 **a)** The daughter nuclide is just the parent minus one alpha particle $\left({}^{4}_{2}\text{He}\right)$. The nuclear reaction for this loss is ${}^{210}_{84}\text{Po} \rightarrow {}^{206}_{82}\text{Pb} + {}^{4}_{2}\text{He}$.

b) The Δm in this reaction is the mass of the daughter atom plus the mass of a helium-4 atom minus the mass of the parent atom; it is -0.0057967 u. The energy released is $-\Delta E = -c^2\Delta m = 5.40$ MeV

c) The kinetic energy of the alpha particle is approximately equal to the energy released, or 8.65×10^{-13} J.

19.10 ${}^{209}_{83}\text{Bi} + {}^{1}_{0}n \rightarrow {}^{210}_{83}\text{Bi}$ ${}^{210}_{83}\text{Bi} \rightarrow {}^{210}_{84}\text{Po} + {}^{0}_{-1}e^{-} + \bar{\nu}$

19.12 **a)** ${}^{209}_{83}\text{Bi} + {}^{64}_{28}\text{Ni} \rightarrow {}^{272}_{111}\text{Rg} + {}^{1}_{0}n$ **b)** ${}^{272}_{111}\text{Rg} \rightarrow {}^{268}_{109}\text{Mt} + {}^{4}_{2}\text{He}$

19.14 **a)** ${}^{4}_{2}\text{He} + {}^{253}_{99}\text{Es} \rightarrow {}^{255}_{101}\text{Md} + 2\,{}^{1}_{0}n$

b) ${}^{249}_{98}\text{Cf} + {}^{10}_{5}\text{B} \rightarrow {}^{257}_{103}\text{Lr} + 2\,{}^{1}_{0}n$

c) ${}^{238}_{92}\text{U} + {}^{12}_{6}\text{C} \rightarrow {}^{244}_{98}\text{Cr} + 6\,{}^{1}_{0}n$

19.16 The mass of each atom minus the sum of the masses of its constituent protons, neutrons, and electrons is the mass change as the atom forms from its constituent particles. This difference in mass is converted from units of mass to units of energy using the knowledge that 1 u (atomic mass unit) is equivalent to 931.494 MeV, and 1 MeV equals 1.602177×10^{-13} J. Binding energies are the negatives of the ΔE's, and the binding energies per nucleon are the binding energies per atom divided by A, the number of protons plus neutrons.

a) For formation of atoms of $^{10}_{4}Be$: the Δm is -0.0697559 u;

$E_b = 64.9772$ MeV per atom $= 6.26935 \times 10^9$ kJ mol^{-1};

binding energy per nucleon = 64.9772/10 = 6.49772 MeV per nucleon.

b) For formation of atoms of $^{35}_{17}Cl$: Δm is -0.3201413 u;

$E_b = 298.210$ MeV per atom $= 28.7729 \times 10^9$ kJ mol^{-1};

binding energy per nucleon = 298.210/35 = 8.52028 MeV per nucleon.

c) For formation of atoms of $^{49}_{22}Ti$: Δm is -0.4582324 u;

$E_b = 426.841$ MeV per atom $= 41.1839 \times 10^9$ kJ mol^{-1};

binding energy per nucleon = 426.841/49 = 8.71104 MeV per nucleon.

19.18 Compare the mass of two $^{16}_{8}O$ atoms to the mass of one $^{32}_{16}S$ atom. The S atom has a smaller mass, so it is more stable. Subtracting the mass of two O atoms from the mass of one S atom gives $\Delta m = -0.0177585$ u.

19.20 Compute the half-life of ^{238}U in minutes

$$t_{1/2} = 4.47 \times 10^9 \text{yr} \times \left(\frac{365 \text{ d}}{1 \text{ yr}}\right) \times \left(\frac{1440 \text{ min}}{1 \text{ d}}\right) = 2.35 \times 10^{15} \text{ min}$$

The activity equals the decay constant of the radioactive nuclide multiplied by the number of nuclides in the sample ($A = \kappa N$). The decay constant equals the half-life divided into the natural logarithm of 2.

$$A = \kappa N = \left(\frac{\ln 2}{t_{1/2}}\right)\left(\frac{0.0010 \text{ g } ^{238}\text{U}}{238 \text{ g mol}^{-1}} \times \frac{6.022 \times 10^{23} \text{atom } ^{238}\text{U}}{1 \text{ mol } ^{238}\text{U}}\right)$$
$$= \left(\frac{0.6931}{2.35 \times 10^{15} \text{ min}}\right)\left(2.53 \times 10^{18} \text{atom } ^{238}\text{U}\right) = 7.5 \times 10^2 \frac{\text{atoms } ^{238}\text{U}}{\text{min}}$$

19.22 **a)** Compute the decay constant of the ^{35}S

$$\kappa = \frac{0.6931}{87.1 \text{ d}} = 0.007958 \text{ d}^{-1}$$

The problem gives the sample's activity, so two of the three quantities in the definition $A = \kappa N$ are known. Compute the third

$$N = \frac{A}{\kappa} = \left(\frac{3.70 \times 10^2 \text{s}^{-1}}{0.00796 \text{ d}^{-1}}\right) \times \left(\frac{86{,}400 \text{ d}^{-1}}{1 \text{ s}^{-1}}\right) = 4.017 \times 10^9$$

The mass of this number of atoms of ^{35}S is

$$m_{^{35}\text{S}} = 4.017 \times 10^9 \text{ atom} \times \left(\frac{1 \text{ mol}^{35}\text{S}}{6.022 \times 10^{23} \text{ atom}}\right) \times \left(\frac{34.97 \text{ g } ^{35}\text{S}}{1 \text{ mol } ^{35}\text{S}}\right) = 2.333 \times 10^{-13} \text{ g } ^{35}\text{S}$$

b) Use the decay constant of the radioactive nuclide; the amount of it that was present to start with and the time elapsed (365 days)

$$N = N_i e^{-kt} = 4.017 \times 10^9 \exp\left[-\left(0.007958 \text{ day}^{-1}\right)\left(365 \text{ day}\right)\right] = 2.200 \times 10^8 \text{ atoms}$$

This number of atoms of ^{35}S is a very small mass, only 1.278 × 10^{-14} g.

19.24 The 1.0 μg of ^{99m}Tc contains 6.08 × 10^{15} atoms, a result obtained by dividing the 1.0 μg by the molar mass of 99 g mol^{-1} and multiplying by Avogadro's number. The 6.0 h half-life is 2.16 × 10^{4} s. Dividing this into ln 2 gives the decay constant $\kappa = 3.21\times10^{-15}\text{s}^{-1}$. The product of the number of atoms and the decay constant is the activity of the sample. It is 2.0 × 10^{11} disintegrations s^{-1}.

19.26 The article contains ^{14}C.

$$A = A_0 \exp(-\kappa t)$$

$$t = \frac{1}{-\kappa}\ln\left(\frac{A}{A_0}\right) = \frac{t_{1/2}}{-\ln 2}\ln\left(\frac{0.0375}{0.255}\right) = \frac{5730 \text{ yr}}{-0.6933}(-1.917) = 15800 \text{ yr}$$

19.28

$$n_{\text{Th decayed}} = \frac{(4.9\times10^{-3}\text{cm}^3 \text{ He})(10^{-3}\text{L cm}^{-3})(1 \text{ atm})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})}\left(\frac{1 \text{ mol Th}}{6 \text{ mol He}}\right) = 3.64\times10^{-8} \text{ mol}$$

$$n_{\text{Th left}} = \frac{7.4\times10^{-3}\text{g}}{232 \text{ g mol}^{-1}} = 3.19\times10^{-5} \text{ mol}$$

$$f_{\text{Th decayed}} = \frac{n_{\text{Th decayed}}}{n_{\text{Th total}}} = \frac{3.19\times10^{-5}}{3.19\times10^{-5} + 3.64\times10^{-8}} = 0.99886$$

Use this fraction in the first-order decay law

$$f = \exp(-\kappa t) \quad \text{gives} \quad \ln f = -\kappa t$$

$$t = \frac{-\ln f}{k} = \frac{-\ln 0.099886}{\ln 2}(t_{1/2}) = \frac{0.00114}{0.69315}(1.39\times10^{10}\text{yr}) = 2.3\times10^{7}\text{yr}$$

The sediment is about 23 million years old.

19.30 From problem **19.29,** the nuclidic ratio $^{238}\text{U}/^{235}\text{U}$ was $N_0 : N_0$ (that is, 1 : 1) when the supernova synthesized the two nuclides 6.02 billion years ago. The earth formed 1.52 billion (6.02-4.50 billion) years after the supernova. To find the nuclidic ratio at that time:

$$\ln\left(\frac{N_{^{235}\text{U}}}{N_0}\right) = -\kappa_{235}(1.52\times10^{9})\text{yr} \text{ and } \ln\left(\frac{N_{^{238}\text{U}}}{N_0}\right) = -\kappa_{238}(1.52\times10^{9})\text{yr}$$

$$\ln\left(\frac{N_{^{238}\text{U}}}{N_{^{235}\text{U}}}\right) = -(\kappa_{238} - \kappa_{235})(1.52\times10^{9})\text{yr}$$

$$\kappa_{238} = \frac{\ln 2}{4.47\times10^{9}\text{yr}} \text{ and } \kappa_{235} = \frac{\ln 2}{7.04\times10^{8}\text{yr}}$$

$$\ln\left(\frac{N_{^{238}\text{U}}}{N_{^{235}\text{U}}}\right) = \ln 2\left(\frac{1}{7.04\times10^{8}\text{yr}} - \frac{1}{4.47\times10^{9}\text{yr}}\right)(1.52\times10^{9})\text{yr}$$

$$\frac{N_{^{238}\text{U}}}{N_{^{235}\text{U}}} = 3.5 \quad \text{when the earth was formed}$$

19.32 Obviously, the decay must occur by positron emission:

$^{13}_{7}\text{N} \rightarrow ^{13}_{6}\text{C} + ^{0}_{1}e^{+} + \nu$ and $^{18}_{9}\text{F} \rightarrow ^{18}_{8}\text{O} + ^{0}_{1}e^{+} + \nu$.

The positrons are very soon annihilated in collisions with electrons in ordinary matter.

19.34 The ^{226}Ra emits more energetic particles and at a greater rate. The emitted particles are moreover absorbed more efficiently. The ^{226}Ra is therefore far more dangerous than the ^{14}C.

19.36 **a)** The number of atoms of ^{239}Pu ingested is

$$N = \left(\frac{5.0\times10^{-6} g}{239 \text{ g mol}^{-1}}\right)\left(6.022\times10^{23} \text{ atoms mol}^{-1}\right) = 1.26\times10^{16} \text{atoms}$$

The activity is

$$A = \kappa N = \frac{N \ln 2}{t_{1/2}} = \frac{\left(1.26\times10^{16}\right)\left(0.6931\right)}{\left(2.411\times10^{4} \text{ yr}\right)\left(365\times24\times60\times60 \text{ s yr}^{-1}\right)}$$
$$= 1.15\times10^{4} \text{ s}^{-1} = 1.15\times10^{4} \text{ Bq}$$

b) The half-life exceeds 20 000 years so the activity drops only negligibly during the first year. The rate of energy emission (the power) from the radionuclide during the first year is

$$P = \left(1.15\times10^{4} \text{ s}^{-1}\right)\left(60\times60\times24\times365 \text{ s yr}^{-1}\right)\left(5.24 \text{ MeV}\right) = 1.90\times10^{12} \text{ MeV yr}^{-1}$$
$$= \left(1.90\times10^{12} \text{ MeV yr}^{-1}\right)\left(1.602\times10^{-13} \text{ J MeV}^{-1}\right) = 0.304 \text{ J yr}^{-1}$$

Each kilogram of tissue receives 1/60 of this, because the worker weighs 60 kg. The dose is

$$\frac{0.304}{60} = 0.0051 \text{ J kg}^{-1} \text{ yr}^{-1} = 5.1 \text{ mGy yr}^{-1}$$

c) Convert this dose to mSv by using the fact that a dose of 1 Gy of alpha radiation is equivalent to 10 Sv. The result is 51 mSv yr^{-1}. This is about fifty times background (1 mSv yr^{-1}), which is enough to cause concern about increased cancer risk, particular lung cancer, but not high enough to say that the dose is *likely* to be lethal. It is far below the LD_{50} level of 5 Gy.

19.38 **a)** The alpha emission of ^{239}Pu is represented $^{239}_{94}\text{Pu} \rightarrow ^{235}_{92}\text{U} + ^{4}_{2}\text{He}$.

b) The Δm in this reaction is -0.0056267 u. Hence, $\Delta E = -5.24$ MeV, and the energy released is +5.24 MeV.

c) The 1.00 g of ^{239}Pu contains 2.52 × 10^{21} atoms of ^{239}Pu. The decay constant is the natural logarithm of 2 divided by the half-life, or 2.876 × 10^{-5} yr^{-1}. The product of these two numbers is the activity: A = 7.25 × 10^{16} yr^{-1}. It is more usual to give activities in reciprocal seconds (becquerels) than in reciprocal years. Dividing by the number of seconds in a year gives A = 2.30 × 10^{9} s^{-1}.

d) Use the equation for the decay of the activity $A = A_i e^{-kt}$ with A_i = 2.30 × 10^{9} s^{-1}, t = 100,000 yr, and κ = 2.876 × 10^{-5} yr^{-1} to find A = 1.30 × 10^{8} s^{-1}. The passage of 100 000 years reduces the activity of a sample of plutonium-239 to about 5.6% of its initial value.

19.40 **a)** $^{6}_{3}\text{Li} + ^{1}_{0}n \rightarrow ^{3}_{1}\text{H} + ^{4}_{2}\text{He}$.

b) The molar mass of the lithium from which the ^{6}Li has been depleted will be larger because ^{6}Li has a smaller atomic mass than the atomic mass of naturally abundant lithium.

19.42 The fusion reaction $2\,{}^{2}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He}$ has $\Delta m = -0.0256003\text{ u}$, a result computed from the masses of the nuclides in text Table 19.1. Compute the change of mass in the reaction of exactly one gram of ${}^{2}_{1}\text{H}$:

$$\Delta m = 1\text{ g }{}^{2}_{1}\text{H} \times \left(\frac{1\text{ mol }{}^{2}_{1}\text{H}}{2.0141078\text{ g }{}^{2}_{1}\text{H}}\right) \times \left(\frac{6.022\times10^{23}\text{atoms}}{1\text{ mol }{}^{2}_{1}\text{H}}\right) \times \left(\frac{-0.0256003\text{ u}}{2\text{ atoms}}\right)$$
$$\times \left(\frac{1.00\times10^{-3}\text{ kg}}{6.022\times10^{23}\text{ u}}\right) = -6.355\times10^{-6}\text{ kg}$$
$$\Delta E = c^2\Delta m = \left(2.9979\times10^{8}\text{ m s}^{-1}\right)^2\left(-6.355\times10^{-6}\text{ kg}\right) = -5.712\times10^{11}\text{ J}$$

The energy release in the fusion of deuterium is 5.712×10^{11} kJ g^{-1} The energy release in the fission of uranium-235 (computed in problem **19.41)** is only $+7.59 \times 10^{7}$ kJ g^{-1}.

19.44 **a)** Two equations are ${}^{231}_{92}\text{U} + {}^{0}_{-1}e^{-} \rightarrow {}^{231}_{91}\text{Pa} + \nu$ and ${}^{231}_{92}\text{U} \rightarrow {}^{231}_{91}\text{Pa} + {}^{0}_{1}e^{+} + \nu$.

b) For the first process,

$$\Delta m = m\left[{}^{231}_{91}\text{Pa}\right] - m\left[{}^{231}_{92}\text{U}\right] = 231.035879 - 231.036289 = -.00041\text{ u}$$

For the second process,

$$\Delta m = m\left[{}^{231}_{91}\text{Pa}\right] + 2m\left[{}^{0}_{1}e^{+}\right] - m\left[{}^{231}_{92}\text{U}\right] = +0.00069\text{ u}$$

Only the first one has $\Delta m < 0$ and is spontaneous.

19.46 Alpha decay decreases Z by 2 and A by 4; beta decay increases Z by 1 and leaves A unchanged. The atomic number of thorium is 90, the atomic number of uranium is 92, and the atomic number of lead is 82. The multi-step process of decay $\text{U} \rightarrow \text{Pb}$ emits two more alpha particles than the process $\text{Th} \rightarrow \text{Pb}$, resulting in a lower A for the lead that derives from it. ${}^{232}_{90}\text{Th}$ loses 232-208 = 24 u (6 α-particles). ${}^{238}_{92}\text{U}$ loses 238-206 = 32 u (8 α-particles).

19.48 Take the system in the 1932 Cockcroft-Walton experiment to consist of the four particles appearing in the balanced nuclear equation. Obtain Δm by subtracting the mass of the reactants from the mass of the products

$$\Delta m = 2m\left[{}^{4}_{2}\text{He}\right] - m\left[{}^{7}_{3}\text{Li}\right] - m\left[{}^{1}_{1}\text{H}\right]$$
$$= 2\left(4.002603250\text{ u}\right) - 7.0160040\text{ u} - 1.007825032\text{ u} = -0.01862253\text{ u}$$

Obtain ΔE by subtracting the initial energies of the particles from the final energies. Assume that the ${}^{7}_{3}\text{Li}$ atom is at rest

$$\Delta E = 700\text{ keV} - 2\left(8.5\text{ MeV}\right) = \left(0.700 - 17.0\right)\text{MeV} = -16.3\text{ MeV}$$

Substitute into the Einstein equation to obtain the speed of light

$$\Delta E = c^2 \Delta m$$
$$-16.3 \text{ MeV}\left(\frac{1.602176\times10^{-13}\text{ J}}{\text{MeV}}\right) = c^2\left(-0.01862253\text{ u}\right)\left(\frac{1.66053886\times10^{-27}\text{ kg}}{\text{u}}\right)$$
$$c^2 = 8.445\times10^{16}\text{ m}^2\text{ s}^{-2}$$
$$c = 2.91\times10^{8}\text{ m s}^{-1}$$

This is within about 3.0% of 2.9979×10^8 m s^{-1}, the speed measured by other means.

19.50 The decay constant for the double beta decay is 1.98×10^{-28} s^{-1}, and $N = 6.022 \times 10^{23}$ atoms. The product of these two values is the activity of the sample. It is $A = 1.2 \times 10^{-4}$ s^{-1}. Only about 10 atoms of ^{82}Se in this big sample decay per day!

19.52 Combine the formulas $A = \kappa N$ and $\kappa = \ln 2/t_{1/2}$; solve for N and substitute the half-life

$$N_{\text{Am}} = \frac{A}{\kappa} = \frac{A\ t_{1/2}}{\ln 2} = \frac{\left(3\times10^{4}\text{ s}^{-1}\right)\left(458\times365\times24\times60\times60\text{ s}\right)}{\ln 2} = 6.25\times10^{14}\text{ atoms}$$
$$m_{\text{Am}} = \left(\frac{6.25\times10^{14}\text{ atoms}}{6.022\times10^{23}\text{ atoms mol}^{-1}}\right)\left(241\text{ g mol}^{-1}\right) = 2.5\times10^{-7}\text{ g}$$

19.54 **a)** According to problem **19.53,** the disintegration rate of ^{14}C atoms in the biosphere is 0.255 Bq^{-1} g^{-1}. The overall activity of the biosphere is 1.1×10^{19} Bq. Use these as follows

$$\frac{1.1\times10^{19}\text{Bq}}{0.255\text{ Bq g}^{-1}} = 4.3\times10^{19}\text{g C}$$

b) The carbon in the earth's crust weighs $(250 \times 10^{-6)}(2.9 \times 10^{25}$ g) = 7.25×10^{21} g. The amount of carbon in the biosphere is only about 0.006 of this or about 0.6%. The rest is tied up in rocks.

19.56 **a)** Equal numbers of atoms of ^{60}Co (half-life: 5.27 yr) and ^{131}I (half-life: 8.04 d) remain in the body indefinitely (for a 70-year lifetime, say). This is long enough for essentially all of these radioactive atoms to decay. Each decay event releases one beta particle, so equal numbers of beta particles are emitted by each nuclide over the lifetime. The *effective* dose from a radionuclide is measured in sieverts (or millisieverts). It differs in general from the *absorbed* dose, which is measured in grays (or milligrays). However both ^{60}Co and ^{131}I emit beta particles. It is reasonable to assume that the difference in the damage that these beta particles inflict comes solely from their differing energies. The ratio of the cumulative effective doses then equals the ratio of the amounts of energy that the two deposit. Assuming that the energies deposited in the body by the two nuclides are proportional to the maximum energy of their beta particles gives

$$\left(\frac{\text{millisieverts from}^{60}\text{Co}}{\text{millisieverts from}^{131}\text{I}}\right)_{\text{long-term}} = \frac{0.32\text{ MeV}}{0.60\text{ MeV}} = 0.53$$

The last assumption in the preceding may be faulty because the distribution curves (as in text Figure 19.4) for the energies of the beta particles from the two radionuclide may have dissimilar shapes.

b) The initial activities of the radionuclides are

$$A_{\text{i}}\left(^{60}\text{Co}\right) = \frac{N_{\text{i}}\ln 2}{t_{1/2}\left(^{60}\text{Co}\right)} \quad \text{and} \quad A_{\text{i}}\left(^{131}\text{I}\right) = \frac{N_{\text{i}}\ln 2}{t_{1/2}\left(^{131}I\right)}$$

Divide the first of these equations by the second

$$\frac{A_i\left({}^{60}\text{Co}\right)}{A_i\left({}^{131}\text{I}\right)} = \left(\frac{N_i\left({}^{60}\text{Co}\right)}{N_i\left({}^{131}\text{I}\right)}\right)\left(\frac{t_{1/2}\left({}^{131}\text{I}\right)}{t_{1/2}\left({}^{60}\text{Co}\right)}\right) = \left(\frac{N_i\left({}^{60}\text{Co}\right)}{N_i\left({}^{131}\text{I}\right)}\right)\left(\frac{8.04\text{ d}}{5.27\times 365\text{ d}}\right)$$

$$= \left(\frac{N_i\left({}^{60}\text{Co}\right)}{N_i\left({}^{131}\text{I}\right)}\right)0.00418$$

The numbers of atoms of the two radionuclides start out equal and stay very nearly equal during the initial hour or so. Therefore, during the initial hour

$$\frac{A\left({}^{60}\text{Co}\right)}{A\left({}^{131}\text{I}\right)} = 0.00418$$

Account for the different energies of the two radionuclides' beta particles in terms of their E_{max}'s, as in part **a**),

$$\left(\frac{\text{millisieverts from}^{60}\text{Co}}{\text{millisieverts from}^{131}\text{I}}\right)_{\text{short-term}} = \left(\frac{0.32\text{ Me V}}{0.60\text{ Me V}}\right)0.00418 = 2.2\times 10^{-3}$$

19.58 Use a series of unit-conversions. Note the inclusion of the efficiency of the process as a conversion factor

$$\text{M}\left[{}^{235}\text{U}\right] = 1\text{ yr}\left(\frac{3.154\times 10^{7}\text{s}}{1\text{ yr}}\right)\left(\frac{10^{9}\text{J}}{1\text{ s}}\right)\left(\frac{100\text{ J generated}}{40\text{ J used}}\right)\left(\frac{1\text{ MeV}}{1.602\times 10^{-13}\text{ J}}\right)$$

$$\times\left(\frac{1\text{atom}^{235}\text{U}}{200\text{ MeV}}\right)\left(\frac{1\text{ mol}}{6.022\times 10^{23}\text{ atoms}}\right)\left(\frac{235\text{ g}}{1\text{ mol}}\right) = 9.6\times 10^{5}\text{g}^{235}\text{U}$$

19.60 The elements Li, Be, and B are lighter that ${}^{12}_{6}\text{C}$, the first stable nuclide formed in helium burning. These elements require other mechanisms for their nucleosynthesis.

19.62 a) $\kappa = \ln 2/t_{1/2}$. Hence

$$0.892 = \exp\left(-\kappa t\right) = \exp\left(\frac{-t\ \ln 2}{t_{1/2}}\right) \quad \text{or} \quad \ln 0.892 = \left(\frac{-t\ \ln 2}{t_{1/2}}\right)$$

Solving for t and using $t_{1/2}$ = 5730 yr gives

$$t\left(\text{tree 1}\right) = -t_{1/2}\left(\frac{\ln 0.892}{\ln 2}\right) = 945\text{ yr} \quad t\left(\text{tree 2}\right) = -t_{1/2}\left(\frac{\ln 0.838}{\ln 2}\right) = 1461\text{ yr}$$

b) Start with ln 0.892 = $-t \ln 2/t_{1/2}$ and solve for $t_{1/2}$. Then use t = 880 yr for the first tree and 1377 yr for the second tree

$$t_{1/2} = -880\left(\frac{\ln 2}{\ln 0.892}\right) = 5.34\times10^{3}\ \text{yr for the first tree}$$
$$t_{1/2} = -1377\left(\frac{\ln 2}{\ln 0.838}\right) = 5.40\times10^{3}\ \text{yr for the second tree}$$

c) The crucial assumption is that the initial activity of ^{14}C in living matter has been constant over the centuries. It might have been *lower* when the old wood was growing. If so: the assumed activity ratios (X/X_0) are too small because X_0 was assumed too large; the actual (X/X_0) is nearer unity and its natural log is smaller; the age is overestimated in a) and the half-life is underestimated in **b)**. If the initial activity was *higher* than the present-day value for growing matter, the opposite situation would hold. The data suggest that the value of X_0 about 1000 years ago was lower than it is now.

19.64 **a)** The ratio A/Z for the elements with even Z from helium (Z = 2) through calcium (Z = 20) is generally quite near to 2. The exceptions are Be, for which the ratio is 2.25, and Ar, for which the ratio is 2.22.

b) The expected atomic mass of argon would be about 36 based on the trend among other Z-even species.

c) Radioactive ^{40}K decays to ^{40}Ar. This enriches argon in the atmosphere with a heavy isotope (compared to what would be found if there were no such decay). This also acts to deplete potassium of its heaviest naturally occurring isotope.

19.66 Calculate the initial activity (rate of disintegration of nuclei) in the radium-226:

$$A = \kappa N = \left(\frac{\ln 2}{1622\ \text{yr}}\right)1.00\ \text{g Ra}\left(\frac{1\ \text{mol Ra}}{226.05\ \text{g Ra}}\right)\left(\frac{6.022\times10^{23}\ \text{atom}}{\text{mmol}}\right) = 1.138\times10^{18}\ \text{yr}^{-1}$$

The rate of release of energy is the product of the energy released per disintegration (decay event) and the rate of the decay events

$$\text{rate} = 4.79\ \text{MeV}\left(\frac{1.602\times10^{-13}\text{J}}{\text{Me V}}\right)\left(1.138\times10^{18}\text{yr}^{-1}\right) = 8.736\times10^{5}\ \text{J yr}^{-1} = 99.7\ \text{J h}^{-1}$$

The energy released over the course of 1.00 h by 1.00 g of ^{226}Ra all goes as heat into 10.0 g of water in a calorimeter at an initial temperature of 25.0°C:

$$q = \left(99.7\ \text{J h}^{-1}\right)\left(1.00\ \text{h}\right) = c_s m\Delta T = \left(4.18\ \text{J K}^{-1}\text{g}^{-1}\right)\left(10.0\ \text{g}\right)\Delta T$$
$$\Delta T = 2.39\ \text{K} = 2.39°\text{C}$$

The final temperature of the water is 27.4 °C.

19.68 **a)** Take the half equation

$$4\ H_3O^+(aq) + 4\ e^- \rightarrow 2\ H_2(g) + 4\ H_2O(l)$$

and subtract the half equation given, leaving

$$Zr(s) + 2\ H_2O(l) \rightarrow ZrO_2(s) + 2\ H_2(g)$$

The $\Delta\varepsilon°$ is 0 - (-1.43 V) = 1.43 V > 0 so the proposed reaction is spontaneous.

b)

$$\log_{10} K = \frac{n}{0.0592\ \text{V}} \Delta\varepsilon° = \frac{4}{0.0592\ \text{V}}(1.43\ \text{V}) = 96.6 \quad \text{from which} \quad K = 4 \times 10^{96}$$

c) The large equilibrium constant in part **b)** means that when zirconium touches water at 25°C, it tends strongly to react to give hydrogen.

Chapter 20

Interaction of Molecules with Light

20.2 From the Beer-Lambert law, the fraction of incident light that is transmitted may be calculated as follows:

$$\begin{aligned}\frac{I_t}{I_o} &= e^{\frac{-N}{V}\sigma\ell} \\ &= e^{[-(6.02\times10^{14}\frac{molecules}{cm^3})(9.25\times10^{-16}\frac{cm^2}{molecule})(1cm)]} \\ &= 0.57\end{aligned}$$

20.4 The relative populations of the *rotational* levels may be calculated as follows:

$$\begin{aligned}\frac{N_1}{N_0} &= \left(\frac{g_1}{g_0}\right)e^{\left[-(\varepsilon_1-\varepsilon_0)/k_BT\right]} \\ &= 3e^{\left[-2\left(60.96\ \text{cm}^{-1}\right)/\left(0.695\ \text{cm}^{-1}\ \text{K}^{-1}\right)\left(300\ \text{K}\right)\right]} \\ &= 1.67\end{aligned}$$

Then the relative populations of the *vibrational* levels may be calculated as follows:

$$\begin{aligned}\frac{N_1}{N_0} &= e^{\left[-(\varepsilon_1-\varepsilon_0)/k_BT\right]} \\ &= e^{\left[-\left(323\ \text{cm}^{-1}\right)/\left(0.695\ \text{cm}^{-1}\ \text{K}^{-1}\right)\left(300\ \text{K}\right)\right]} \\ &= 0.212\end{aligned}$$

20.6 Computer the reduced mass and from it the moment of inertia of the diatomic molecule

$$\mu = \frac{(1.007825)(18.9984)\ \text{u}}{1.007825+18.9984}\times\left(1.66054\times10^{-27}\ \text{kg u}^{-1}\right) = 1.589\times10^{-27}\ \text{kg}$$

$$I = \mu R_e^2 = \left(1.589\times10^{-27}\ \text{kg}\right)\left(0.926\times10^{-10}\ \text{m}\right)^2 = 1.363\times10^{-27}\ \text{kg m}^2$$

The energy spacing is

$$\Delta E = \frac{h^2}{8\pi^2 I}\left[1(2)-0(1)\right] = \frac{\left(6.6269\times10^{-34}\text{ J s}\right)^2}{4\pi^2\left(1.363\times10^{-47}\text{kg m}\right)^2} = 8.16\times10^{-22}\text{ J}$$

20.8 **a)** The average interval between rotational lines is $0.623\times10^{12}\text{ s}^{-1} = h/4\pi^2 I$

$$I = \frac{h}{4\pi^2\left(0.623\times10^{12}\text{ s}^{-1}\right)} = \frac{6.626\times10^{-34}\text{J s}}{4\pi^2\left(0.623\times10^{12}s^{-1}\right)} = 2.69\times10^{-47}\text{kg m}^2$$

b) The allowed absorption frequencies for $0\rightarrow J$ transitions

$$\nu = \frac{h}{8\pi^2 I}\left[J\left(J+1\right)-0\right] = \frac{h}{8\pi^4 I}\frac{J\left(J+1\right)}{2}$$

$$0\rightarrow1 \quad \nu = 1\times0.623\times10^{12}\text{ s}^{-1} \quad \Delta E = h\nu = 4.13\times10^{-22}\text{ J}$$
$$0\rightarrow2 \quad \nu = 3\times0.623\times10^{12}\text{ s}^{-1} \quad \Delta E = h\nu = 1.24\times10^{-21}\text{ J}$$
$$0\rightarrow3 \quad \nu = 6\times0.623\times10^{12}\text{ s}^{-1} \quad \Delta E = h\nu = 2.48\times10^{-21}\text{ J}$$

c) Use nuclidic masses from text Table 19.1 to get the reduced mass μ

$$\mu = \frac{\left(1.0078\text{ g mol}^{-1}\right)\left(34.969\text{ g mol}^{-1}\right)\left(10^{-3}\text{ kg g}^{-1}\right)}{\left(1.0078+34.969\text{ g mol}^{-1}\right)\left(6.022\times10^{23}\text{ mol}^{-1}\right)} = 1.627\times10^{-27}\text{ kg}$$

$$R_e = \left(I/\mu\right)^{1/2} = 1.29\times10^{-10}\text{ m} = 1.29\text{ Å}$$

d) The absorptions are the $3\rightarrow4, 4\rightarrow5, 5\rightarrow6,$ and $6\rightarrow7$ transitions.

20.10 First calculate the moment of inertia and then substitute for the reduced mass to calculate the equilibrium bond length.

$$I = \frac{h}{8\pi^2 c\tilde{B}} = 4.16\times10^{-46}\text{kg}\cdot\text{m}^2$$
$$R_e = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{4.16\times10^{-46}\text{kg}\cdot\text{m}^2}{5.81\times10^{-27}\text{kg}}}$$
$$= 2.67\text{ Å}$$

20.12 The population of energy level E_i relative to energy level E_f is

$$\frac{P_i}{P_f} = \frac{g_i}{g_f}e^{-\left(E_i-E_f\right)/\kappa_B T}$$

The rotational energy levels are

$$E_J = J\left(J+1\right)\frac{h^2}{8\pi^2 I} \quad J = 0, 1, 2,\ldots$$

and the degeneracy is $2J + 1$. The population of energy level E_J relative to the population of the energy level E_0 (the ground state) is therefore

$$\frac{P_J}{P_0} = gJ^{e^{-J(J+1)h^2/8\pi^2 I\kappa T}}$$

Evaluate the part of the exponential factor that recurs in the three calculations

$$\frac{h^2}{8\pi^2 I\kappa T} = \frac{\left(6.626\times10^{-34}\,\text{J s}\right)^2}{8\pi^2\left(66.8\times10^{-47}\ \text{kg m}^2\right)\left(1.38\times10^{-23}\ \text{J K}^{-1}\right)\left(298.15\ \text{K}\right)} = 2.01\times10^{-3}$$

Note that all the units cancel away. The exponential factor of each term is $e^{J(J+1)(0.00201)}$.
The specific relative populations are

a) $P_5/P_0 = (2\cdot5+1)\exp\left(-(5)(6)(0.00201)\right) = 11e^{-0.060} = 10.4;$

b) $P_{25}/P_0 = (2\cdot25+1)\exp\left(-(25)(26)(0.00201)\right) = 51e^{-1.31} = 13.8;$

c) $P_{15}/P_0 = (2\cdot15+1)\exp\left(-(15)(16)(0.00201)\right) = 31e^{-0.482} = 19.1.$

Rotational energy levels above the ground state are significantly populated at room temperature. Rotational spectra will consequently include transitions for which $J_i > 0$. The rotational distribution extends to higher values of J here than it does in problem **20.9** because the separation between rotational levels for N_2O is smaller than it is for NaH, the subject of problem **20.9**. The smaller separation is due to N_2O's larger moment of inertia.

20.14 Compute the frequency of the line in the IR spectrum of Na_2 and the reduced mass of the molecule

$$\nu = \frac{c}{\lambda} = \frac{2.998\times10^{8}\ \text{m s}^{-1}}{6.28\times10^{-5}\ \text{m}} = 4.77\times10^{12}\ \text{s}^{-1}$$

$$\mu = \frac{\left(22.9898\ \text{g mol}^{-1}\right)\left(22.9898\ \text{g mol}^{-1}\right)\left(10^{-3}\ \text{kg g}^{-1}\right)}{\left(2\times22.9898\ \text{g mol}^{-1}\right)\left(6.022\times10^{23}\ \text{mol}^{-1}\right)} = 1.91\times10^{-26}\ \text{kg}$$

Substitute these values in the equation for the frequency of a simple harmonic oscillator

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}}$$

$$\kappa = \mu(2\pi\nu)^2 = \left(1.91\times10^{-26}\ \text{kg}\right)\left(2\pi\times4.77\times10^{12}\ \text{s}^{-1}\right)^2 = 17.2\ \text{kg s}^{-2}$$

This is smaller than the force constant of the bond in Li_2 (in problem **20.13**). The bond in Na_2 is springier because the atoms are larger and farther apart.

20.16

$$\nu = \frac{c}{\lambda} = \frac{2.998\times10^{8}\ \text{m s}^{-1}}{2.9\times10^{-6}\ \text{m}} = 1.03\times10^{14}\ \text{s}^{-1}$$

$$\kappa = \mu(2\pi\nu)^2 = \frac{1.008\ \text{u}}{6.022\times10^{23}\ \text{u kg}^{-1}}\left(2\pi\times1.03\times10^{14}\text{s}^{-1}\right) = 7.1\times10^{2}\ \text{kg s}^{-2}$$

This is almost 40% greater than the C—H force constant; the N—H bond is stiffer.

20.18 The energy difference is

$$\Delta E = h\nu = \left(6.626\times10^{-34}\ \text{J s}\right)\left(1.15\times10^{13}\ \text{s}^{-1}\right) = 7.62\times10^{-21}\ \text{J}$$

$$\frac{P_i}{P_j} = \exp\left[\frac{-\Delta E}{\kappa_B T}\right] = e^{-1.84} = 0.159$$

For every 1.00×10^6 molecules in the ground state, there are $0.159 \times 10^6 = 1.59 \times 10^5$ molecules in the first excited state.

20.20 The reduced masses of N_2, CO, and O_2 are comparable to one another, the ratio of the vibrational frequencies of N_2 and CO to that of O_2 is close to $\frac{3}{2}$, suggesting that N_2 and CO have triple bonds and that O_2 has a double bond. We can estimate the bond order of H_2 by calculating the ratios of the force constants and vibrational frequencies as follows.

$$\frac{k_{H_2}}{k_{N_2}} = \left(\frac{\mu_{H_2}}{\mu_{N_2}}\right)\left(\frac{\nu_{N_2}^2}{\nu_{H_2}^2}\right)$$
$$= \left(\frac{0.5}{7}\right)\left(\frac{2331^2}{4160^2}\right)$$
$$= 0.23$$

Suggesting the bond order of H_2 is one.

$$k_{H_2} = \mu_{H_2}\left(2\pi\nu_{H_2}\right)^2 = \mu_{H_2}\left(2\pi c\tilde{\nu}_{H_2}\right)^2$$
$$= \left(0.5 \text{ amu}\right)\left(1.66\times10^{-27} \text{ kg}\cdot\text{amu}^{-1}\right)\left[2\pi\left(3\times10^{10} \text{ cm}\cdot\text{s}^{-1}\right)\left(4160 \text{ cm}^{-1}\right)\right]^2$$
$$= 510 \text{ N}\cdot\text{m}$$

$$k_{N_2} = \mu_{N_2}\left(2\pi\nu_{N_2}\right)^2 = \mu_{N_2}\left(2\pi c\tilde{\nu}_{N_2}\right)^2$$
$$= \left(7 \text{ amu}\right)\left(1.66\times10^{-27} \text{ kg}\cdot\text{amu}^{-1}\right)\left[2\pi\left(3\times10^{10} \text{ cm}\cdot\text{s}^{-1}\right)\left(2331 \text{ cm}^{-1}\right)\right]^2$$
$$= 2243 \text{ N}\cdot\text{m}$$

$$k_{CO} = \mu_{CO}\left(2\pi\nu_{CO}\right)^2 = \mu_{CO}\left(2\pi c\tilde{\nu}_{CO}\right)^2$$
$$= \left(6.8 \text{ amu}\right)\left(1.66\times10^{-27} \text{ kg}\cdot\text{amu}^{-1}\right)\left[2\pi\left(3\times10^{10} \text{ cm}\cdot\text{s}^{-1}\right)\left(2143 \text{ cm}^{-1}\right)\right]^2$$
$$= 1856 \text{ N}\cdot\text{m}$$

$$k_{O_2} = \mu_{O_2}\left(2\pi\nu_{O_2}\right)^2 = \mu_{O_2}\left(2\pi c\tilde{\nu}_{O_2}\right)^2$$
$$= \left(8 \text{ amu}\right)\left(1.66\times10^{-27} \text{ kg}\cdot\text{amu}^{-1}\right)\left[2\pi\left(3\times10^{10} \text{ cm}\cdot\text{s}^{-1}\right)\left(1550 \text{ cm}^{-1}\right)\right]^2$$
$$= 1133 \text{ N}\cdot\text{m}$$

20.22

$$\nu\left({}^{12}C-{}^{13}C\right) = \left[\sqrt{\mu\left({}^{12}C-{}^{12}C\right)/\mu\left({}^{12}C-{}^{13}C\right)}\right]\left[1053 \text{ cm}^{-1}\right]$$
$$= \left[\sqrt{6/6.24}\right]\left[1053 \text{ cm}^{-1}\right]$$
$$= 1033 \text{ cm}^{-1}$$

20.24 The $C-F$ and $C-Cl$ bonds in CCl_2F_2 are the most polar bonds represented in this group of molecules, thus, they will infrared radiation more strongly than the others.

20.26 The two molecules are very similar to one another as are their infrared spectra. The broad band in the 3300 – 3600 cm^{-1} region of the lower spectrum is the characteristic O – H stretch of an alcohol so that spectrum belongs to 2-methyl-1-butanol.

20.28 The spectrum will have two peaks, one for the chemically equivalent group of 4 protons on the benzene ring and one for the chemically equivalent group of 6 protons on the two methyl groups. The areas of the peaks will have ratio 1 : 1.5 or 4 : 6.

20.30 The NMR spectrum of compound A shows four sets of peaks. The triplet near $\delta = 1$ (relative intensity = 3), and the doublet near $\delta = 1.75$ (relative intensity = 2) are characteristic of adjacent methyl and ethyl groups, respectively, suggesting the presence of of a $–CH_2CH_3$ group.. The chemical shift of the doublet near $\delta = 4$ (relative intensity = 2) is characteristic of a $–CH_2$ group bonded to an oxygen atom and the chemical shift of the single peak near $\delta = 8$ is characteristic of a hydrogen atom bonded to a carbon atom of a carbonyl group. The molecule is propyl formate $CH_3CH_2CH_2COOH$.

The NMR spectrum of compound B shows three sets of peaks. The triplet near $\delta = 1$ (relative intensity = 3), and the doublet near $\delta = 2.25$ (relative intensity = 2) are characteristic of adjacent methyl and ethyl groups, respectively, suggesting the presence of an ethyl group. The chemical shift of the $–CH_2$ group suggests that it is bonded to the carbon atom of a carbonyl group. The single peak near $\delta = 3.75$ (with relative intensity = 3) is characteristic of a methyl group bound to the oxygen atom of an ester. The molecule is methyl proprionate $CH_3CH_2COOCH_3$.

The NMR spectrum of compound C shows three sets of peaks. The triplet near $\delta = 1.25$ (relative intensity = 3) is characteristic of a methyl group bonded to an aliphatic $–CH_2$ group and the quartet near $\delta = 4.1$ (relative intensity = 2) is characteristic of a $–CH_2$ group bonded to an aliphatic $–CH_3$ group as well as an oxygen atom. The single peak near $\delta = 2$ (relative intensity = 3) is characteristic of a methyl group bonded to a carbonyl carbon atom. The molecule is ethyl acetate $CH_3COOCH_2CH_3$.

20.32 The absorption coefficient and cell length were kept constant in this experiment. Under these circumstances the Beer-Lambert law states that a graph of the absorbance A of the light-absorbing species versus its concentration c will give a straight line. The problem quotes values of percent transmissions. Divide them by 100 to obtain the transmittance T. By definition, $A = - \ln T$. Plot $- \ln T$ versus the concentrations. The result is a straight line with a slope of 0.408 mL μg^{-1}. Note that c is given in μg mL^{-1}, not in mol L^{-1}. Substitute $T = 0.35$ into the standardization equation

$$-\ln T = \left(0.408\ \mu\text{g mL}^{-1}\right)c \quad \text{from which} \quad c = 2.57\ \mu\text{g mL}^{-1}$$

20.34

$$\begin{aligned}
A &= c_{\text{tryp}} \in_{\text{tryp}} \ell + c_{\text{tyro}} \in_{\text{tyro}} \ell \\
&= \left(2 \times \frac{1.0\text{ g L}^{-1}}{26{,}000\text{ g mol}^{-1}}\right)\left(5690\text{ L cm}^{-1}\text{ mol}^{-1}\right)\left(1.0\text{ cm}\right) \\
&\quad + \left(6 \times \frac{1.0\text{ g L}^{-1}}{26{,}000\text{ g mol}^{-1}}\right)\left(1280\text{ L cm}^{-1}\text{ mol}^{-1}\right)\left(1.0\text{ cm}\right) \\
&= 0.733 = -\ln T \\
T &= 0.480 \quad \text{corresponding to 48\% transmittance}
\end{aligned}$$

20.36 The electron lost in the ionization of C_2H_4 will be from a bonding π orbital because the π system in C_2H_4 is less than half filled, a fact that assures that all of the π electrons are bonding electrons (in the ground state of the molecule). The bond order between the two carbons in $C_2H_4^+$ is 3/2, less than that in C_2H_4.

20.38 Crystal violet is violet, which implies that it absorbs the color that is the complement of violet, namely yellow. This means it has a maximum in its absorption near 590 nm.

20.40 The π electrons in naphthalene are more delocalized in both the ground state and the excited states than the π electrons in benzene, but the energy of the orbitals are lowered more in the excited state than in the ground state. This shifts the maximum absorption of light to a wavelength longer than 255 nm.

20.42 Compute the energy of dissociation of the I—Cl bond

$$\begin{aligned}\Delta E &= \Delta H - RT\Delta n_g = \Delta H - RT \\ &= 211\times10^3\ \text{J mol}^{-1} - \left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\left(298\ \text{K}\right) \\ &= 2.09\times10^5\ \text{J mol}^{-1} = 3.46\times10^{-19}\ \text{J}\end{aligned}$$

The maximum wavelength of light capable of supplying this much energy is

$$\lambda_{\max} = \frac{hc}{\Delta E} = \frac{\left(6.626\times10^{-34}\ \text{J s}\right)\left(2.998\times10^8\ \text{m s}^{-1}\right)}{3.46\times10^{-19}\ \text{J}} = 5.74\times10^{-7}\ \text{m} = 574\ \text{nm}$$

20.44 The energy of the bonds (330 kJ mol^{-1}) is equivalent to 5.48 × 10^{-19} J per bond. Using $E = hc/\lambda$ gives $\lambda = 3.62\times10^{-7}$m. This is 362 nm.

20.46 Carbon dioxide and sulfur dioxide have similar formulas, but quite different molecular structures. Carbon dioxide is a linear molecule. In it, the central C forms s bonds to the two oxygen atoms using *sp* hybrid orbitals. These bonds are joined by *p* bonds from the overlap of C-atom 2*p* and O-atom 2*p* orbitals. The central atom in CO_2 has no lone pairs. The molecule of SO_2 is a bent molecule. The central S is sp^2 hybridized: two of these orbitals overlap with orbitals of the O's in s bonds and the third accommodates a lone pair. Thus, the *SN* of the central S is 3. The molecule is bent with an O—S—O angle near 120°. One 3*p* orbital of the S mixes with one 2*p* orbital from each of the O's in a π-system.

20.48

$$E = \frac{hc}{\lambda} = 2.84\times10^{-19}\text{J} = 171\ \text{kJ}$$

This is a little short of 5 times 34.5 kJ, so at most 4 molecules of ATP could be produced per photon.

20.50 The bond stretches as the NaCl molecule rotates faster. This changes its moment of inertia. Figure out the reduced mass

$$\mu = \frac{\left(22.9898\ \text{g mol}^{-1}\right)\left(34.9689\ \text{g mol}^{-1}\right)\left(10^{-3}\ \text{kg g}^{-1}\right)}{\left(22.9898+34.9689\ \text{g mol}^{-1}\right)\left(6.022142\times10^{23}\ \text{mol}^{-1}\right)} = 2.30328\times10^{-26}\ \text{kg}$$

The frequency of light absorbed in the $1\rightarrow2$ rotational transition is

$$\nu = \frac{h}{8\pi^2\mu R_e^2}\left[2(3)-1(2)\right] = \frac{h}{2\pi^2\mu R_e^2}$$

Solve for the bond length in terms of ν and substitute the given ν's

$$R_e = \sqrt{\frac{h}{2\pi^2\mu\nu}} = \sqrt{\frac{6.6260688\times10^{-34}\ \text{J s}}{2\pi^2\left(2.30328\times10^{-26}\ \text{kg}\right)}\left(\frac{1}{\nu}\right)}$$

$$R_{e\,(n=0)} = 2.37142\times10^{-10}\ \text{m} = 2.37142\ \text{Å}$$

$$R_{e\,(n=1)} = 2.38166\times10^{-10}\ \text{m} = 2.38166\ \text{Å}$$

20.52 The ratio of probabilities is

$$\frac{P_i}{P_j} = \exp\left[\frac{-\Delta E}{\kappa_B T}\right]$$

Taking $\Delta E = 2\times10^{-5}$ kJ mol^{-1} $= 3.32\times10^{-26}$ J gives

$$\frac{P_i}{P_j} = \exp\left(-8.07\times10^{-6}\right) = 1.00$$

The populations are almost equal. The same result holds if $\Delta E = 2\times10^{-4}$ kJ mol^{-1}.

20.54 The electron in ethylene is excited from a π to a π^* orbital. The transfer reduces the overall bond order of the the molecule by 1. The C to C bond in the molecule in the excited state should be *longer* than it was in the ground state. Because the bond is weaker, its force constant, κ, is diminished, and the vibrational frequency of the C to C stretching mode is reduced.

20.56 **a)** Excitation of the electron in H_2^+ to an antibonding orbital will lead to the dissociation of the molecule. The effect of an antibonding electron is to oppose the continued association of the nuclei.

b) If even more energy is fed into a H_2^+ molecule, the electron can be brought into a higher-level bonding molecular orbital. The molecule should persist for a while in this bound state, but it will also eventually dissociate to H and H^+.

20.58 For sulfuric acid

$$S + O_2 \rightarrow SO_2 \qquad SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3 \qquad SO_3 + H_2O \rightarrow H_2SO_4$$

For nitric acid

$$N_2 + O_2 \rightarrow 2\,NO \qquad NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad NO_2 + OH \rightarrow HNO_3$$

20.60 The term "greenhouse effect" refers to the increase in the average temperature at the Earth's surface that arises from the trapping of solar energy by the atmosphere. It is caused by the presence in the atmosphere of gases such as carbon dioxide, water vapor, and methane. These gases (greenhouse gases) allow incoming (visible) sunlight to pass through to the surface but absorb the infrared (heat) radiation emitted by the surface. The effect has been heightened in recent decades by heavy releases of greenhouse gases, in particular CO_2, from human activity. CO_2 is released by the combustion of natural gas, coal, and fuel oil for electrical power and for home heating and by the combustion in gasoline in automobiles. Energy sources that do not produce greenhouse gases include solar cells, nuclear power plants, wind-driven generators, and hydroelectric plants.

23.62 The energy should be lowered, because the two energy levels will split into an unoccupied upper level and an occupied lower level.

20.64

$$A_{\mathrm{HIn}} = 0.142 \quad a_{\mathrm{HIn}} = \frac{0.142}{6.36\times10^{-4}} = 223$$
$$A_{\mathrm{In^-}} = 0.943 \quad a_{\mathrm{In^-}} = \frac{0.943}{6.36\times10^{-4}} = 1483$$

Let [HIn] equal the concentration of HIn in the solution with I = 0.02 and let [In$^-$] equal the concentration of In$^-$ in the same solution. Then

$$\left[\mathrm{HIn}\right] = 6.36\times10^{-4} - \left[\mathrm{In^-}\right]$$
$$0.470 = 223\left[\mathrm{HIn}\right] + 1483\left[\mathrm{In^-}\right]$$

Substituting the first equation into the second and solving give

$$\left[\mathrm{In^-}\right] = 2.60\times10^{-4} \quad \text{and} \quad \left[\mathrm{HIn}\right] = 3.76\times10^{-4}$$

At a pH of 8.207, $\left[\mathrm{H_3O^+}\right] = 6.21\times10^{-9}$ so that

$$K = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{In^-}\right]}{\left[\mathrm{HIn}\right]} = \frac{\left(6.21\times10^{-9}\right)\left(6.21\times10^{-9}\right)}{3.76\times10^{-4}} = 4.29\times10^{-9}$$

Taking the logarithm gives pK_a = 8.368. Repeating the calculation at the other four values of ionic strength gives

I	0.02	0.04	0.06	0.08	0.10
pK_a	8.37	8.36	8.36	8.36	8.36

20.66 The concentrations are

$$\left[\mathrm{CO}\right] = \frac{P_{\mathrm{CO}}}{RT} = 4.0\times10^{-11}\ \mathrm{mol\ L^{-1}} \quad \text{and} \quad \left[\mathrm{CH_4}\right] = \frac{P_{\mathrm{CH_4}}}{RT} = 6.8\times10^{-10}\ \mathrm{mol\ L^{-1}}$$

$$\begin{aligned}\frac{d\left[\mathrm{OH}\right]}{dt} &= -\kappa_{\mathrm{CO}}\left[\mathrm{CO}\right]\left[\mathrm{OH}\right] - \kappa_{\mathrm{CH_4}}\left[\mathrm{CH_4}\right]\left[\mathrm{OH}\right]\\ &= -\left(1.6\times10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}}\right)\left(4.0\times10^{-11}\ \mathrm{mol\ L^{-1}}\right)\left[\mathrm{OH}\right]\\ &\quad -\left(3.8\times10^{9}\ \mathrm{L\ mol^{-1}\ s^{-1}}\right)\left(6.8\times10^{-10}\ \mathrm{mol\ L^{-1}}\right)\left[\mathrm{OH}\right]\\ &= -9.0\ \mathrm{s^{-1}}\left[\mathrm{OH}\right] = -\kappa_{\mathrm{eff}}\left[\mathrm{OH}\right]\end{aligned}$$

The effective rate constant κ_{eff} is 9.0 s^{-1}. The half-life is ln 2/κ_{eff}, which is 0.077 s.

Chapter 21

Structure and Bonding in Solids

21.2 **a)** A cereal box does *not* have four-fold rotational symmetry since no two perpendicular edges are equal in length.

b) A stop sign (octagonal in shape) does have a four-fold rotational axis of symmetry (perpendicular to the plane of the sign).

c) A tetrahedron (solid with equivalent equilateral triangles at its sides) does *not* have a four-fold axis of symmetry; it does have four different three-fold axes.

d) A cube has three four-fold rotational axes (passing through the centers of its three pairs of parallel faces).

21.4 The symmetry elements of the PF_5 molecule are one 3-fold axis of rotation (through the axial F atoms), three 2-fold axes of rotation (through the P atom and the equatorial F atoms), one horizontal plane of symmetry (reflection), and three vertical symmetry planes (reflection).

21.6 Substitute 2θ, λ, and n in the (rearranged) Bragg law:

$$d = \frac{n\lambda}{2\ \sin\theta} = \frac{2\left(1.237\ \text{Å}\right)}{2\ \sin\left(35.58/2\right)} = 4.049\ \text{Å}$$

21.8 Rearrange the Bragg law and substitute:

$$\sin\theta = \frac{n\lambda}{2d} = \frac{2\left(1.539\ \text{Å}\right)}{2\left(4.28\ \text{Å}\right)} = 0.3596 \quad \text{from which} \quad \theta = 21.076° \text{ and } 2\theta = 42.2°$$

21.10 Write the Bragg law as $\sin\theta = n\lambda/2d$ and substitute the given values of λ and d. This gives $\sin\theta = 0.07160n$. Diffracted beams are to be found at 2θ's corresponding to integral values of n. The answers are

n	$\sin\theta$	2θ	n	$\sin\theta$	2θ	n	$\sin\theta$	2θ
1	0.07160	±8.21°	6	0.4296	±50.88°	11	0.7876	±103.9°
2	0.1432	±16.47	7	0.5012	±60.16	12	0.8592	±118.4
3	0.2148	±24.81	8	0.5728	±69.89	13	0.9308	±137.1
4	0.2864	±33.28	9	0.6444	±80.24	14	1.0024	–
5	0.3580	±41.95	10	0.7160	±91.45			

The ±'s appear because if angle q fulfills the Bragg law, then angle $\left(180° - \theta\right)$ does too. This gives rise to possible reflections at $2\theta = \left(360° - 2\theta\right) = -2\theta$. These reflections come from the other side of the layers of atoms. There are thus 13×2 or 26 possible diffracted beams of this wavelength from this set of planes. If $n \geq 14$ then sin $\theta > 1.00$, and θ is not defined.

21.12 The formula for the volume of a general parallelepiped is in the text. It is

$$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

The crystal is monoclinic, so $\alpha = \gamma = 90^\circ$. The cosine of 90° is zero, hence, using the trigonometric identity $\sin^2\beta + \cos^2\beta = 1$:

$$V = abc\sqrt{1 - \cos^2\beta} = abc\sin\beta$$

Substitution gives $V = 589\ \text{Å}^3$ for the unit cell of potassium hexacyanoferrate(III).

21.14 Calculate the volume of the unit cell of strontium chloride hexahydrate by substituting in

$$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

with the understanding that in a trigonal cell $a = b = c$ and $\alpha = \beta = \gamma$. Substitution of the given a and a give

$$V = 678.413\ \text{Å}^3 = 678.413 \times 10^{-24}\ \text{cm}^3$$

The molar mass of $SrCl_2 \cdot 6H_2O$ is 266.617 g mol^{-1}. A mole of unit cells of this crystal weighs 3 times this amount because there are 3 formula units per cell. The volume of a mole of unit cells is the volume of a single cell multiplied by Avogadro's number. Hence:

$$\rho = \frac{3 \times 266.617\ \text{g mol}^{-1}}{\left(678.413 \times 10^{-24}\ \text{cm}^3\right)\left(6.022 \times 10^{23}\ \text{mol}^{-1}\right)} = 1.958\ \text{g cm}^{-3}$$

The measured density of $SrCl_2 \cdot 6H_2O$ is 1.93 g cm^{-3}.

21.16 Imagine 1 cm^3 of iron at room conditions. Its mass is 7.86 g. Figure the mass of the Fe atoms in the sample in atomic mass units (u):

$$m_{\text{Fe}} = 1\ \text{cm}^3\left(\frac{10^{24}\ \text{Å}^3}{\text{cm}^3}\right)\left(\frac{1\ \text{unit cell}}{2.87^3\ \text{Å}}\right)\left(\frac{2\ \text{Fe atoms}}{\text{unit cell}}\right)\left(\frac{55.847\ \text{u}}{1\ \text{Fe atom}}\right) = 4.7248 \times 10^{24}\ \text{u}$$

The ratio of the mass of a sample of a substance in u to its mass in grams is Avogadro's number

$$N_{\text{A}} = \frac{4.7248 \times 10^{24}\ \text{u}}{7.86\ \text{g}} = 6.01 \times 10^{23}\ \text{u g}^{-1}$$

21.18 Calculate the volume of the unit cell of turquoise by substitution of α = 68.61°, β = 69.71°, γ= 65.08°, a = 7.424 Å, b = 7.629 Å, and c = 9.910 Å into the formula

$$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma} = 461.4\ \text{Å}$$

Now, imagine a (mammoth!) turquoise that contains one mole of unit cells. Its volume is

$$461.4\ \text{Å}^3 \times \left(\frac{1\ \text{cm}^3}{10^{24}\ \text{Å}^3}\right) \times 6.022 \times 10^{23} = 277.86\ \text{cm}^3$$

The mass of the stone is its volume multiplied by its density (2.927 g cm^{-3}) or 813.3 g. This is the mass of a mole of unit cells of turquoise. Obtain the formula mass of turquoise by adding up the contributions of the several elements in the formula given in the problem. It is 813.44 g mol^{-1}. Since $813.3 \approx 813.44$, every unit cell contains one formula unit. There is one Cu atom per formula unit, so every unit cell contains one Cu atom.

21.20 A unit cell has eight corners, but each is shared by a total of eight cells, so it contributes $\frac{1}{8}\times 8 = 1$ Ca atom per unit cell. There is one Ti atom at each cell center. There are six faces, each shared by two unit cells, so there are $\frac{1}{2}\times 6 = 3$ oxygen atoms per unit cell. The chemical formula is $CaTiO_3$.

21.22 **a)** Metallic aluminum has four atoms per unit cell *(n* in the following).

b)

$$V_m = N_A a^3 = \frac{n\mathcal{M}}{\rho} = \frac{4\times 26.98 \text{ g mol}^{-1}}{2.70 \text{ g cm}^{-3}}$$

$$a = \sqrt[3]{\frac{4\times 26.98 \text{ g mol}^{-1}}{6.022\times 10^{23} \text{ mol}^{-1}\times 2.70 \text{ g cm}^{-3}}} = 4.05\times 10^{-8} \text{ cm}$$

$$d = \frac{a\sqrt{2}}{2} = 2.86\times 10^{-8} \text{ cm}^3$$

21.24 **a)**

$$V_m = N_A a^3 = \frac{n\mathcal{M}}{\rho} = \frac{4\times 58.69 \text{ g mol}^{-1}}{8.90 \text{ g cm}^{-3}}$$

$$a = \sqrt[3]{\frac{4\times 58.69 \text{ g mol}^{-1}}{6.022\times 10^{23} \text{ mol}^{-1}\times 8.90 \text{ g cm}^{-3}}} = 3.525\times 10^{-8} \text{ cm}$$

The Ni atoms touch along the face diagonal of the unit cell so the nearest neighbor distance is $\frac{1}{2}$ of the face diagonal

$$d = \frac{a\sqrt{2}}{2} = 2.49\times 10^{-8} \text{ cm}$$

b) Four Ni radii cover the face diagonal, whose length is $\sqrt{2}$ times the cell edge. This makes the radius of a Ni atom $\left(\sqrt{2}a/4\right)$, which is 1.25×10^{-8} cm.

c) An interstitial site (hole) of octahedral symmetry lies at the center of the unit cell in Ni, at coordinates $\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a$ if a corner of the unit cell is taken as the origin. Each unit cell also shares additional, equivalent sites with neighboring cells for a total of four octahedral holes per cell. The maximum radius of an atom in an octahedral hole in Ni is

$$r = \frac{a}{2} - \frac{a\sqrt{2}}{4} = a\left(\frac{1}{2} - \frac{\sqrt{2}}{4}\right) = \left(3.525\times 10^{-8} \text{ cm}\right)\left(0.14645\right) = 0.516\times 10^{-8} \text{ cm}$$

Each unit has also has eight holes of tetrahedral symmetry, $\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a$ and symmetry-related locations. The maximum radius of an atom to fit in a tetrahedral hole in Ni is 0.280×10^{-8} cm, which is quite small. The structure also contains trigonal holes, which are even smaller.

21.26 Take the host atom radius to be r_1 and the interstitial atom radius to be r_2. Then from Table 21.2

$r_1 = \frac{\sqrt{3}}{4}a$, where a is the lattice parameter (the edge length of the cubic unit cell).

An interstitial hole at the center of a face could come in contact either with the atom at the center of the cell, or with the four atoms at the corners of the face. The first possibility requires

$$2r_1 + 2r_2 \le a \text{ and the second requires that } 2r_1 + 2r_2 \le \sqrt{2a}$$

which uses the fact that the face diagonal is $\sqrt{2}a$. Clearly the first condition is the stronger one, so the maximum interstitial radius is

$$r_2 = \frac{a}{2} - r_1 = \left(\frac{1}{2} - \frac{\sqrt{3}}{4}\right)a$$

The radius ratio is

$$\frac{r_2}{r_1} = \frac{\left(\frac{1}{2} - \frac{\sqrt{3}}{4}\right)a}{\left(\frac{\sqrt{3}}{4}\right)a} = \left(\frac{1}{2} - \frac{\sqrt{3}}{4}\right)\frac{4}{\sqrt{3}} = \frac{2}{\sqrt{3}} - 1 = 0.155$$

21.28 **a)** Rb is metallic. **b)** C_5H_{12} is molecular. **c)** B is covalent. **d)** Na_2HPO_4 is ionic.

21.30 If the boiling point of pentane is slightly less than the melting point of rubidium, then the melting point of pentane is certainly less than the melting point of rubidium. Moreover, rubidium must be a low-melting metal because the boiling point of a molecular liquid like pentane is low. Boron, a covalent substance, has the highest melting point, and the sodium hydrogen phosphate therefore has the second highest melting point.

21.32 Sugar crystals melt at a much lower temperature than salt crystals. A melt of salt crystals is a good conductor of electricity, while a solution or melt of sugar crystals conducts electricity only poorly (molten sugar will char, but this is a chemical distinction). An aqueous solution of salt is a much better electrical conductor than an aqueous solution of sugar. The refractive indices and densities of the two differ; sugar is optically active but salt is not, the crystal habits of the two differ

21.34 The nearest neighbors of a Na^+ ion are 6 Cl^- ions. The second nearest neighbors are a set of 12 Na^+ ions. The third nearest neighbors are a set of 8 Cl^- ions.

21.36 The presence of Schottky defects (vacancies) means that the measured density of a real crystal will inevitably be less than density of a hypothetical ideal crystal having no vacancies. This will cause estimates of Avogadro's number by the method of problem 21.15 and 21.16 to be high because the computation requires division by the density.

21.38 **a)** The empirical formula of the nickel oxide is $Ni_{0.9796}O$. (The answer $NiO_{1.0208}$ is equivalent.) The formula is determined by comparing the relative number of moles of Ni and O in a sample of any arbitrary size. Note that the mass percentage of O is 21.77%.

b) For every 1 mol of O atoms in the sample, there is 0.9796 mol of Ni atoms. If y mol of Ni is in the +3 oxidation state then $(0.9796 - y)$ mol is in the +2 oxidation state. The total positive charge on the nickel atoms is $3y + 2(0.9796 - y)$ mol. The total negative charge on the O atoms is –2 mol. These charges must add up to zero to maintain electrical neutrality

$$\left(3y+2\left(0.9796-y\right)\right)\text{ mol}-2\text{ mol}=0$$

Solving for y gives 0.0408 mol. The fraction of Ni in the +3 state is 0.0408/0.9796 = 0.0416.

21.40 The lattice energy in this problem is the energy required to separate 1.00 mol of RbCl(s) into its component ions. Use text equation 21.3 to compute the negative of the electrostatic potential energy among the ions in their equilibrium positions

$$\begin{aligned}-V &= 1.00\text{ mol}\frac{1.7627\times\left(1.602\times10^{-19}\text{ C}\right)^2\times6.022\times10^{23}\text{ mol}^{-1}}{4\pi\times8.854\times10^{-12}\text{ C}^2\text{ J}^{-1}\text{ m}^{-1}\times3.48\times10^{-10}\text{ m}}\\ &= 7.04\times10^5\text{ J}=704\text{ kJ}\end{aligned}$$

This result only approximates the lattice energy. A 10% reduction to account for the short-range repulsive interactions and zero-point energy gives a better estimate

$$\text{lattice energy} = 633\text{ kJ}$$

21.42 **a)** Obtain the lattice energy by adding the changes in internal energy in the following five reactions[2]

$$\begin{array}{ll}\text{KBr}(s)\rightarrow\text{K}(s)+\tfrac{1}{2}\text{Br}_2(l) & \Delta E_1\approx-\Delta H_f^\circ\left(\text{KBr}(s)\right)=393.80\text{ kJ}\\ \tfrac{1}{2}\text{Br}_2(l)\rightarrow\text{Br}(g) & \Delta E_2\approx\Delta H_f^\circ\left(\text{Br}(g)\right)=111.88\text{ kJ}\\ \text{K}(s)\rightarrow\text{K}(g) & \Delta E_3\approx\Delta H_f^\circ\left(\text{K}(g)\right)=89.24\text{ kJ}\\ \text{Br}(g)+e^-\rightarrow\text{Br}^-(g) & \Delta E_4=-EA(\text{Br})=-324.7\text{ kJ}\\ \text{K}(g)\rightarrow\text{K}^+(g)+e^- & \Delta E_5=IE_1(\text{K})=418.8\text{ kJ}\\ \hline \text{KBr}(s)\rightarrow\text{K}^+(g)+\text{Br}^-(g) & \Delta E_{\text{lattice}}\approx689.0\text{ kJ}\end{array}$$

Taking close account of the distinction between ΔE and ΔH gives 684.1 kJ, which differs by less than 1%.

b)

$$\begin{aligned}\text{lattice energy}=-V &= \frac{(1.7476)\left(1.602\times10^{-19}\text{ C}\right)^2\left(6.022\times10^{23}\text{ mol}^{-1}\right)}{4\pi\left(8.854\times10^{-12}\text{ C}^2\text{ J}^{-1}\text{ m}^{-1}\right)\left(3.298\times10^{-10}\text{ m}\right)}\\ &= 7.361\times10^5\text{ J mol}^{-1}=736.1\text{ kJ mol}^{-1}\end{aligned}$$

This is somewhat (7-8%) too large because of the neglect of repulsive forces.

21.44 The Bragg law is written for each of the two experiments, the first with x-rays of wavelength $\lambda_1 = 1.54$ Å and the second with x-rays of unknown wavelength λ_2. The ratio of the second to the first is

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[2] The lattice energy is a change in internal energy ($a\ \Delta U$). It is represented here as a ΔE for the sake of consistency with the text.

$$\frac{n_1\lambda_1}{n_2\lambda_2} = \frac{d_1 \sin\theta_1}{d_2 \sin\theta_2}$$

But $n_1 = n_2, d_1 = d_2,$ and λ_1 and $2\theta_1$ and $2\theta_2$ are given. It follows that $\lambda_2 = 1.65$ Å.

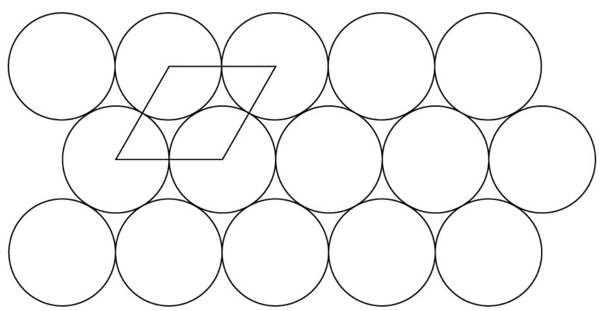
21.46 In x-ray diffraction, the greatest possible scattering angle 2θ is 180°, which corresponds to direct back-scattering. When 2θ is 180°, θ is 90° and sin θ is 1.00. Substitute this into the Bragg law with n = 1 and d = 4.20 Å. The value of λ is 8.40 Å. If the wavelength of the probing x-rays exceeds the dimension of the feature being probed (the distance between the parallel planes) by more than a factor of two, no diffraction can occur.

21.48 **a)** Substitute the given data into the Bragg law and compute $d = 3.344$ Å.

b) The volume of the unit cell of polonium is d^3 because the distance between the parallel faces of the unit cell is the cell edge. The contents of the unit cell are a single Po atom because there is only one lattice point per cell and there must be an atom of Po for every lattice point. Also, the mass of a Po atom is 209 u. The density of Po is therefore $209 \text{ u}/(3.344 \text{ Å})^3 = 5.59 \text{ u Å}^{-3}$. This converts to 9.28 g cm^{-3}. The density tabulated in Appendix F is close: 9.32 gem^{-3}.

21.50 The problem gives the number of atoms of each kind in the unit cell. The unit cell is the repeating motif of the crystalline substance, so its contents have the same ratio of atoms as the substance. There is 1 O atom per unit cell (1/8 atom per corner times 8 corners), 1 Cl atom (entirely within the cell), and there are 3 Na atoms ($\frac{1}{2}$ atom per face times 6 faces). The formula is Na_3ClO. This substance exists; the answer is not a mix-up with sodium chlorate.

21.52 The closest possible packing arrangement for disks in a plane is



Let the radius of the disks equal r. Then their area is πr^2. The smallest possible unit cell is shown. It is a rhombus having sides of length $2r$ and interior angles of 60° and 120°. Each unit cell contains one disk. Then

$$A_{\text{cell}} = 2r\left(2r \sin 60°\right) = 4\frac{\sqrt{3}}{2}r^2 = 2\sqrt{3}r^2$$

$$\text{Packing fraction} = \frac{\pi r^2}{2\sqrt{3}r^2} = 0.907$$

This is just a cross section through the cylindrical fibers which must therefore have the same packing fraction.

21.54 The 2.570 Å nearest-neighbor distance in LiCl(s) is an Li^+—Cl^- distance. It is $\frac{1}{2}$ of the length of the edge of the f.c.c. cubic unit cell. Compute the shortest Cl^-—Cl^- distance, which lies along the face diagonal of the cell. It equals $\sqrt{2}(2.570 \text{ Å}) = 3.63 \text{ Å}$, which is very close to twice the radius of the Cl^- ion (see text Appendix F). If the Li^+—Cl^- distance got any shorter in LiCl(*s*), then the Cl^-—Cl^- distance would have to be less than the sum of the ions' radii. The energetic cost to force the ions to overlap would be prohibitive. In contrast, Cl^-—Cl^- repulsions do not exist in LiCl(*g*) molecules. The Li^+—Cl^- distance can drop to 2.027 Å as the bond gains covalent character.

21.56 Write equations for the reactions under comparison

$$CuCl_2(s) \rightarrow CuCl(s) + \tfrac{1}{2}Cl_2(g) \qquad \Delta G° = \Delta H° - T\Delta S° > 0$$
$$CuBr_2(s) \rightarrow CuBr(s) + \tfrac{1}{2}Br_2(l) \qquad \Delta G° = \Delta H° - T\Delta S° > 0$$
$$CuI_2(s) \rightarrow CuI(s) + \tfrac{1}{2}I_2(s) \qquad \Delta G° = \Delta H° - T\Delta S° < 0$$

Only the third reaction is spontaneous under room conditions; so only it has a negative $\Delta G°$. Negative $\Delta G°$ is favored by a positive $\Delta S°$ and negative $\Delta H°$. Iodine is solid in its standard state at 298 K; bromine is liquid; chlorine is gaseous. The $\Delta S°$ terms for the decomposition of $CuCl_2$(*s*) and $CuBr_2$(*s*) accordingly *favor* the change. But the decomposition is spontaneous only for CuI_2(*s*). It follows that the $\Delta H°$ term must dominate in determining the sign of $\Delta G°$. Contrive a Born-Haber type route from reactants to products:

$$CuX_2(s) \rightarrow Cu^{2+}(g) + 2X^-(g) \qquad \Delta H_1^0 \qquad\qquad X(g) \rightarrow \tfrac{1}{2}X_2(g) \qquad \Delta H_4^0$$
$$Cu^{2+}(g) + e^- \rightarrow Cu^+(g) \qquad \Delta H_2^0 \qquad\qquad \tfrac{1}{2}X_2(g) \rightarrow \tfrac{1}{2}X_2(g,\ l, \text{ or } s) \qquad \Delta H_5^0$$
$$X^-(g) \rightarrow X(g) + e^- \qquad \Delta H_3^0 \qquad\qquad Cu^+(g) + X^-(g) \rightarrow CuX(s) \qquad \Delta H_6^0$$

It is easily verified that these six steps add up to the correct equation for the decomposition. Examine the signs of the different ΔH^0*'s* and the effect that changing X from Cl to Br to I) has on their magnitudes.

ΔH_2^0 is large and negative but need not be considered in the comparison because it is the same for all three compounds (X does not appear in the equation). ΔH_3^0 is positive (equal to the election affinity of X). It is larger (more positive) for Cl and Br than it is for I. This trend favors the instability of CuI_2(*s*) relative to the others. ΔH_4^0, however, works in the opposite direction. It is less negative for I than for Br and Cl because of the weakness of the bond in I_2. ΔH_5^0 is negative for I because of the attractions between I_2 in the solid; it is less negative for Br and zero for X = Cl or F. This trend favors the greater instability for CuI_2(*s*)

Now for the two lattice enthalpies: ΔH_1^0 is positive and ΔH_6^0 is negative. ΔH_6^0 is almost certainly smaller in magnitude than ΔH_1^0 because of the smaller charge on copper. The larger the anion the larger the interionic distance and the smaller the magnitude of the lattice energy. This trend favors lower stability for the CuI_2(*s*) compared to the other halides.

Overall, three factors favor greater instability for CuI_2(*s*): the lower electron affinity of I, the greater attractions between I_2 molecules in the solid state, and the larger size of the I^- ion, which reduces the magnitude of its lattice enthalpy. The magnitudes of the various enthalpy changes can be estimated from data in text Appendix F, Table 3.2, and Appendix D. It seems likely that the last effect (the change in lattice enthalpy with ionic size) is the largest one.

21.58 a)

$$D = D_0 \exp\left[-E_a/RT\right]$$
$$= \left(0.145 \text{ cm}^2 \text{ s}^{-1}\right)\exp\left[-\frac{42220 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(370.95 \text{ K}\right)}\right] = 1.65\times10^{-7}\text{cm}^2 \text{ s}^{-1}$$

b)

$$\overline{\Delta x^2} = 6Dt = 6\left(1.65\times10^{-7}\text{cm}^2 \text{ s}^{-1}\right)\left(60\times60 \text{ s}\right)$$
$$\left(\overline{\Delta x^2}\right)^{\frac{1}{2}} = 6.0\times10^{-2} \text{ cm} = 0.60 \text{ mm}$$

21.60 **a)** covalent **b)** covalent within the chains, but molecular between chains **c)** partially covalent along long chains of alternating atoms (—Si—O—Si—). The chains are themselves negatively charged and bonded ionically to positive ions. **d)** metallic.

21.62 The octahedral site will give rise to an octahedral crystal field splitting of the *d*-orbitals on the Cr^{3+}. Because Cr^{3+} is a d^3 species, its electron configuration will be $(t_{2g})^3$, with a single electron in each of the lower-energy, t_{2g}, orbitals.

21.64 The violet color of the fluorite (as seen in Fig. 21.30) shown must arise from absorption of the complementary color, yellow. From Fig. visible light spectrum, the maximum absorption should be near 590 nm.

Chapter 22

Inorganic Materials

22.2 The Lewis dot structure of the cyclosilicate ion displays a total of 144 valence electrons. It consists of 6 Si and 6 O atoms alternating in a ring. Each Si atom has 2 other O's linked to it as side-groups on the ring. All bonds are single.

22.4 **a)** Tremolite consists of infinite double chains. All O's are in the -2 oxidation state, and all Si's in the +4 state. The Mg and Ca are both +2 and the hydrogen is +1. The assignment to a structural type is made on the basis of the ratio of silicate oxygen to silicon, which is 2.75 to 1.

b) Gillespite consists of infinite sheets. The Si and O are in the +4 and -2 oxidation states respectively (as they are in all the silicate minerals in this problem) and the Ba and Fe are both +2.

c) Uvarovite contains silicate tetrahedra. The Ca is in the +2 state, and the Cr is in the +3 state.

d) Barysilate contains pairs of silicate tetrahedra. The Mn and Pb are both in the +2 oxidation state.

22.6 **a)** The aluminosilicate mineral amesite derives formally from a silicate with a 5 to 2 oxygen-to-silicon ratio. Based on this ratio it contains infinite sheets of aluminosilicate units. The aluminum is in the +3 oxidation state, the Si and O are in the +4 and -2 states, respectively. This is true in all the aluminosilicates in this problem. The Mg is in the +2 state and the "other aluminum" (that which is not part of the silicate framework) is +3 aluminum. The hydroxide hydrogen and hydroxide oxygen are +1 and -2 respectively.

b) Phlogopite contains infinite sheets of aluminosilicate units. The K is +1 and the Mg is +2. Other atoms are as before.

c) Thomsonite contains an infinite network of aluminosilicate units. The Na and Ca are +1 and +2 respectively, and the Al and Si are +3 and +4.

22.8

$$\underbrace{3\ Al_2Si_4O_{10}(OH)_2(s)}_{\text{pyrophyllite}} \rightarrow \underbrace{Al_6Si_2O_{13}(s)}_{\text{mullite}} + \underbrace{10\ SiO_2(s)}_{\text{cristobalite}} + 3\ H_2O(g)$$

22.10 The dehydration of kaolinite ($Al_2Si_2O_5(OH)_4$) produces 2 mol of water per mol of the mineral. The molar mass of kaolinite is 258 g mol^{-1}. The chemical amount of kaolinite is its mass divided by its molar mass. Doubling this gives the chemical amount of steam, 31.0 mol. This quantity is inserted in the ideal-gas equation with T = 873.15 K and P = 1 atm. The answer is 2.2×10^3 L.

22.12 Imagine a 100 g sample of Portland cement and compute the masses of the several oxides. Then obtain the chemical amounts of the oxides by dividing each mass by the proper molar mass. The formulas of the oxides then allow computation of the chemical amounts of the six elements and the total chemical amount of oxygen. Put everything on a basis of 1.00 mol of O. The answer can then be summarized in the "chemical formula" $Ca_{0.514}Si_{0.158}Al_{0.052}Fe_{0.016}Mg_{0.028}S_{0.010}Na_{0.020}O_{1.00}$.

22.14 The slaking of lime is represented

$$\mathrm{CaO}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{Ca(OH)_2}(s)$$

The $\Delta H°$ for this reaction at 298.15 K is

$$\Delta H^\circ_{298} = 1(-986.09) - 1(-635.09) - 1(-285.83) = -65.17 \text{ kJ}$$

Slaking 1 mol (56.08 g) of CaO(*s*) is exothermic to this extent. Slaking 1.00 kg releases proportionately more heat, 1162 kJ. This is only an estimate because the product is unlikely to be solid $Ca(OH)_2$ when lime is slaked under ordinary conditions. Dissolution of some of the $Ca(OH)_2(s)$ releases more heat.

22.16 The sum of the oxidation states of the single atoms must equal zero. The oxidation states of Tl, Ca, Ba and O are +3, +2, +2 and -2 respectively. Let the oxidation state of Cu be *y*. Then:

$$(2 \times 3) + (2 \times 2) + (2 \times 2) + (3y) + (10.5 \times -2) = 0 \text{ and } y = \tfrac{7}{3} = 2.33$$

22.18 **a)** $\mathrm{BCl_3}(g) + \mathrm{NH_3}(g) \rightarrow \mathrm{BN}(s) + 3\ \mathrm{HCl}(g)$

b) For this reaction

$$\Delta H° = 1(-254.4) + 3(-92.31) - 1(-403.76) - 1(-46.11) = -81.46 \text{ kJ}$$

Thus, the $\Delta H°$ per mole of BN(*s*) is -81.46 kJ mol^{-1}.

c) Boron nitride has extremely low electrical conductivity and a very high melting point. It is nearly as hard as diamond.

22.20 The oxidation of $B_4C(s)$ is

$$\mathrm{B_4C}(s) + 4\ \mathrm{O_2}(g) \rightarrow 2\ \mathrm{B_2O_3}(s) + \mathrm{CO_2}(g)$$

The ΔG°_{298} of this reaction is computed from ΔG°_f's in the usual way (taking additional data from Appendix D)

$$\Delta G^\circ_{298} = 2(-1193.70) + 1(-394.36) - 4(0) - 1(-71) = -2711 \text{ kJ}$$

Boron carbide is thermodynamically unstable in oxygen at standard conditions and thermodynamically unstable in air as well. It reacts only slowly, however.

22.22 a)

$$\text{resistivity} = \rho = \frac{1}{\sigma} = \frac{1}{4.3\times10^{7}\ \Omega^{-1}\text{m}^{-1}} = 2.33\times10^{-8}\ \Omega\ \text{m}$$

$$\text{resistance} = R = \frac{\ell}{A}\rho = \frac{(1.5\ \text{m})(2.33\times10^{-8}\ \Omega\ \text{m})}{\pi(2.0\times10^{-3}\ \text{m})^2} = 2.78\times10^{-3}\ \Omega = 0.0028\ \Omega$$

b) $I = V/R = 0.070\ \text{V}/2.78\times10^{-3}\ \Omega = 25\ \text{A}$

$J = I/A = 25\ \text{A}\Big/\pi(2.0\times10^{-3}\text{m})^2 = 2.0\times10^{6}\ \text{A m}^{-2}$

c) $E = V/\ell = 0.070\ \text{V}/1.5\ \text{m} = 0.047\ \text{V m}^{-1}$

22.24 The acetate ion CH_3COO^- is hydrogen bonded to nearby water molecules. It must either break these bonds to move or carry the water molecules with it. Either effect reduces its ionic mobility relative to Cl^- ion.

22.26 Adding Ni to the pure Cu creates defects that serve as scattering centers for the electrons. As the number of such centers increases, the mobility of electrons decreases and the resistivity increases.

22.28 In each case the maximum wavelength is calculated by setting the band-gap energy equal to hc/λ. For GaAs, it is 867 nm; for CdS, it is 512 nm. The former is in the infrared region of the spectrum; this latter is near the middle of the visible region of the spectrum. Cameras need to be sensitive to visible light only.

22.30 Put E_g on a molar basis (multiply by N_A) and substitute into the equation that appears in problem **22.29**

$$\begin{aligned} n_e &= (4.8\times10^{15}\text{cm}^{-3}\text{K}^{-3/2})T^{3/2}e^{-E_g/2RT} \\ &= (4.8\times10^{15}\text{cm}^{-3}\text{K}^{-3/2})(300\ \text{K})^{3/2}e^{-(6.62\times10^{4}\ \text{J mol}^{-1})/2(8.3145\ \text{J K}^{-1}\text{mol}^{-1})(300\ \text{K})} \\ &= 4.3\times10^{13}\ \text{cm}^{-3} \end{aligned}$$

22.32 **a)** Ge doped with In is a *p*-type semiconductor, **b)** CdS doped with As is a *p*-type semiconductor if As substitutes for S. If As substitutes at random for Cd or S then it raises the number of electrons in the product and makes it *n*-type.

22.34 Substitute the band gap energy of the LED into the equation $E = hc/\lambda$ and compute the required wavelength. It is 584 nm, in the yellow region of the visible spectrum.

22.36 The decrease in band-gap energy that goes with the conversion of cinnabar to metacinnabar is accompanied by a shift in the wavelength corresponding to excitation across the band gap of the pigment from 621 nm (in cinnabar) to 764 nm. The bright crimson of the cinnabar fades away. In the first case, red light with wavelengths longer than 621 nm is transmitted and the pigment appears red; in the second case, all colors of visible light are absorbed and the sample appears black.

22.38 The formula of the $Si_{12}O_{30}^{12-}$ ion is six times the formula of the $Si_2O_5^{2-}$ unit. The structure should contain infinite sheets. The oxidation state of Si is +4, of O is -2, of H is +1, of Cl is -1, and of Mg is +2. Combining these gives a total oxidation number for the remaining $Mn_{12}Fe$ unit of +26. Thus both the Mn and the Fe must be in the +2 oxidation state.

22.40 The Na^+ ion and Ca^{2+} ion have nearly the same radius (0.98 and 0.99 Å). They substitute freely in each other's sites in solid solutions of albite and anorthite. The radius of the K^+ ion is greater (1.33 Å) and its substitution in sites in albite and anorthite is restricted.

22.42 The given quantities define the zeolite $K_2O \cdot Al_2O_3 \cdot 4(SiO_2) \cdot 6(H_2O)$. This compound is 9.91% Al by mass.

22.44 **a)** The reaction is $SiO_2(quartz) \rightarrow SiO_2(cristobalite)$.

$$\Delta H^\circ_{298} = (1\text{ mol})(-909.48\text{ kJ mol}^{-1}) - (1\text{ mol})(-910.94\text{ kJ mol}^{-1}) = 1.46\text{ kJ}$$
$$\Delta S^\circ_{298} = (1\text{ mol})(42.68\text{ J K}^{-1}\text{ mol}^{-1}) - (1\text{ mol})(41.84\text{ J K}^{-1}|\text{ mol}^{-1}) = 0.84\text{ J K}^{-1}$$
$$\Delta G^\circ_{298} = (1\text{ mol})(-855.43\text{ kJ mol}^{-1}) - (1\text{ mol})(-856.67\text{ kJ mol}^{-1}) = 1.24\text{ kJ}$$

b) The conversion *quartz* → *cristobalite* has a positive ΔG°_{298}, the reverse conversion has a negative ΔG°_{298}. This means that quartz is favored over cristobalite at 298.15 K.

c) Assuming that ΔS° for the reaction *quartz* → *cristobalite* stays positive as the temperature goes up, then at a high enough temperature cristobalite will be favored.

22.46 Soda-lime glass is an amorphous solid of approximate composition 73% SiO_2, 17% Na_2O, 5% CaO, and 5 % MgO. It contains little aluminum. Fired kaolinite contains a great deal of aluminum, having the approximate composition $Al_6Si_2O_{13}$. Soda-lime glass contains a random, three-dimensional ionic network $(SiO_3^{2-})_n$ the charge of which is locally neutralized by the Na+, Ca^{2+} and Mg^{2+} ions. Fired kaolinite includes Al as part of structural aluminosilicate chains. Fired kaolinite has undergone an irreversible chemical reaction; its physical shape is unalterable without breakage. Glass can be melted and reformed.

22.48 Magnesia (MgO) is an O^{2-} donor and is a basic refractory. Silica is an O^{2-} acceptor and is an acidic refractory. The two react: $MgO + SiO_2 \rightarrow MgSiO_3$.

22.50 In acid: $BeO(s) + 2\ H_3O^+(aq) + H_2O(l) \rightarrow Be(H_2O)_4^{2+}(aq)$.

In base: $BeO(s) + 2\ OH^-(aq) + H_2O(l) \rightarrow Be(OH)_4^{2-}(aq)$.

22.52 The oxide ceramics are in general thermodynamically stable with respect to their constituent elements. The nonoxide ceramics are often *not* thermodynamically stable with respect to reaction to form oxides (as in air).

22.54 The band gap becomes larger going from a metal to a semiconductor to an insulator.

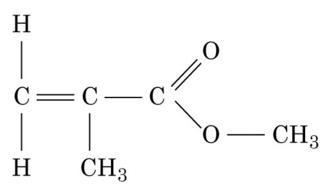
22.56 The conductivity of the Sb-doped Si (an n-type semiconductor) should decrease as Ga is added to a minimum when the ratio of the dopants is 1 to 1. At this point the doubly-doped Si is electronically equivalent to pure silicon itself. More Ga beyond this point should make the conductivity increase, as the semiconductor becomes p-type.

Chapter 23

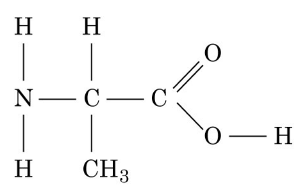
Polymeric Materials and Soft Condensed Matter

23.2 $n\ C_2F_4 \rightarrow \left(CF_2CF_2\right)_n$.

23.4 Polymethyl methacrylate forms by addition polymerization of methyl methacrylate, which has the structure:



23.6 The starting monomer, which is alanine, has the structure:



23.8 The repeating unit in the polyester has the formula $C_{10}H_8O_4$. This formula is the sum of the molecular formulas of terephthalic acid and ethylene glycol minus twice the formula of water, a relationship that derives from the fact that the one molecule of diacid condenses with one molecule of diol with loss of two molecules of water. The molar mass of the repeating unit is 192.17 g mol^{-1}. The number of moles of repeating unit needed is

$$n = 10.0 \times 10^3 \text{ g polymer} \times \left(\frac{1 \text{ mol units}}{192.17 \text{ g polymer}}\right) = 52.04 \text{ mol}$$

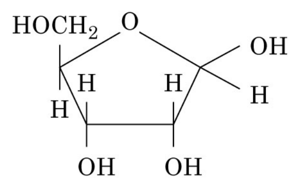
This means that the synthesis needs 52.04 mol of terephthalic acid $\left(\mathcal{M} = 166.13 \text{ g mol}^{-1}\right)$ and 52.04 mol of ethylene glycol $\left(\mathcal{M} = 62.07 \text{ g mol}^{-1}\right)$. These chemical amounts convert to 8.65 kg of terephthalic acid and 3.23 kg of ethylene glycol.

23.10 The mass of polystyrene is 2.84×10^{12} g, and the mass of a monomer unit of styrene (C_8H_8) is 104.2 g mol^{-1}. In addition polymerization, no mass is lost by the splitting out of small molecules. Hence, 2.73×10^{10} mol of styrene was incorporated, which is 1.64×10^{34} molecules (by multiplication by Avogadro's number).

23.12 Smectic phases involve the lining up of molecules in layers. They might tend to form if the center of one molecule is strongly attracted to the center of another. By lying in a single plane, the centers have a stronger attraction for one another, and lower energy.

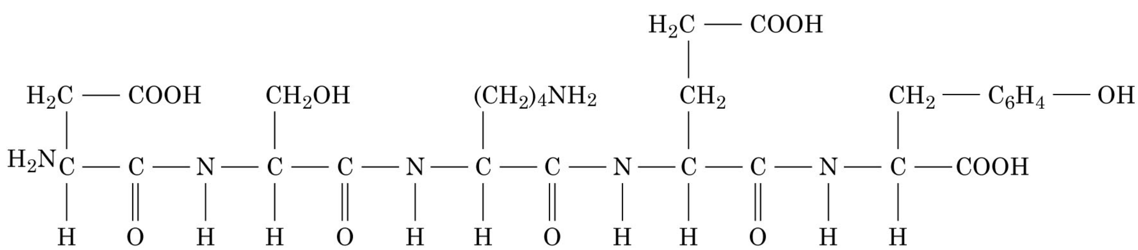
23.14 In terms of molecular packing, a cylinder is intermediate between a sphere and a flat layer. Thus, cylindrical rolls should form at compositions intermediate between those at which spherical micelles form and those at which planar layers form.

23.16 The ring form of D-ribose has four asymmetric carbon atoms:



23.18 There are $20^{10} = 1.0 \times 10^{13}$ possible polypeptides containing 10 amino acids. There are $20^{100} = 1.3 \times 10^{130}$ possible polypeptides containing 100 amino acids.

23.20 The pentapeptide is



Most of the side-groups are polar. The compound should be more soluble in water than in octane.

23.22 A nucleotide consists of a molecule of deoxyribose ($C_5H_{10}O_4$), a molecule of phosphoric acid (H_3PO_4) and a molecule of one of the four bases (adenine ($C_5H_5N_5$), cytosine ($C_4H_5N_3O$), thymine ($C_5H_6N_2O_2$), and guanine ($C_5H_5N_5O$)) linked as a unit by the loss of two molecules of water. The average molar mass of a nucleotide is 327 g mol^{-1}. The links between nucleotides form with the loss of still another molecule of water, so the average molar mass of the repeating unit in a DNA molecule is 309 g mol^{-1}. If the molar mass of a particular DNA is 4×10^9 g mol^{-1}, its molecule contains 1.3×10^7 nucleotides. The answer changes if the amounts of the four nucleotides are not approximately equal.

23.24 The polymerization reaction must be driven by an increase in entropy in the surroundings, because it proceeds itself with a local decrease in entropy. Heat must therefore be evolved into the surroundings; the reaction is exothermic.

23.26 If the only difference between natural rubber and gutta-percha is the geometrical relationship (*cis* in natural rubber, but *trans* in gutta-percha) at the recurring double bonds, then conversion of the double bonds to single bonds by reaction with H_2 should give identical products.

23.28 The structure of L-sucrose is the mirror of the sucrose image in Figure 23.16.

23.30 Imagine 1.00 mol of hemoglobin. It weighs 65 000 g and contains 223.6 g of Fe. This much Fe is 4.0 mol of Fe. Each mole of hemoglobin contains 4.0 mol of Fe, so each molecule of hemoglobin contains 4 atoms of Fe.

23.32 TGAACTGGC

23.34 The number of different two-letter words (two-base codons) possible with four letters (two bases) is only $4^2 = 16$.